Recent Advances in the Palladium Catalyzed Suzuki-Miyaura Cross-Coupling Reaction in Water

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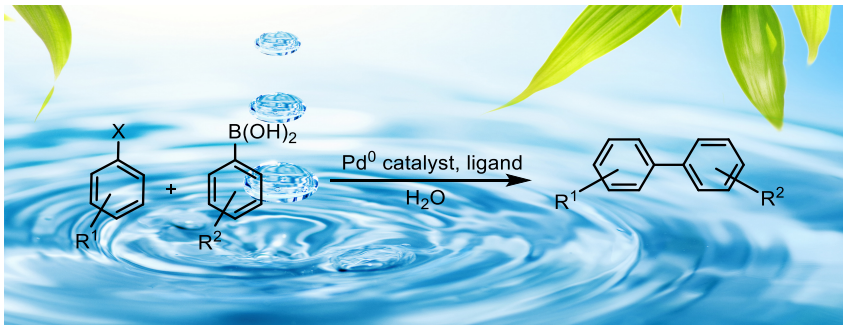
Graphical Abstract



Abstract

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of organic halides with boronic acids is one of the most versatile methods for the synthesis of biaryls. Green chemistry is a rapidly developing new field that provides us a proactive avenue for the sustainable development of future science and technologies. When designed properly, clean chemical technology can be developed in water as a reaction medium. The technologies generated from such green chemistry endeavors may often be cheaper and more profitable. This review covers the literature on palladium-catalysed the Suzuki-Miyaura cross-coupling reaction in water.

Keywords: Cross-coupling, Palladium, Aqueous catalysis, Green chemistry, Sustainable chemistry

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1 Introduction

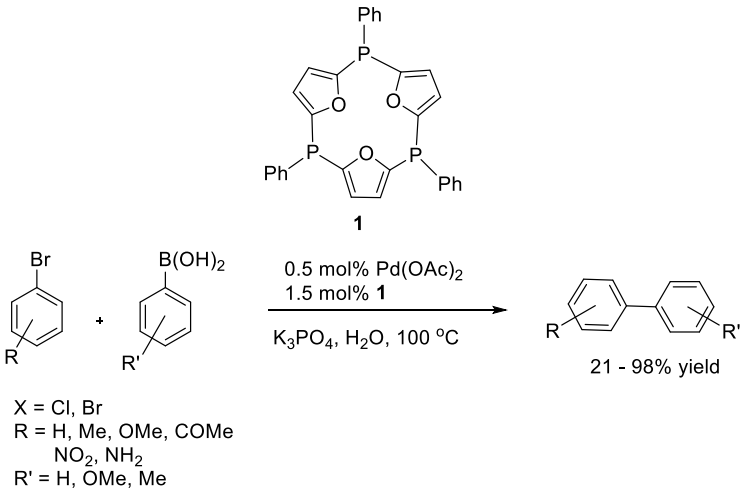
The Suzuki-Miyaura cross-coupling reaction (SMC hereafter) is one of the most important synthetic transformations developed in the 20th century.[1, 2] This is one of the most versatile methods for the synthesis of biaryls and alkene derivatives. These are structural constituents of numerous agrochemicals, natural products, pharmaceuticals, and polymers.[2–5] Several reviews on the SMC have been published in the literature.[6–11] Recently, green chemistry awareness attempts to address the environmental impact of both chemical products and the processes by which these are produced.[12, 13] Around 80% of the chemical waste from a reaction mixture corresponds to the solvent. Water is commonly considered as a benign solvent in view of its non-toxicity and abundant natural occurrence. The use and release of "clean water" will have the least impact to the environment.[14] In the case of the SMC, the stability of boronic acids in aqueous solvent are viewed as advantageous compared to other cross-coupling reactions to be performed in water. The literature on the SMC in water up to 2010 has been reviewed by Polshettiwar *et al*.[15] Herein, we focus on the use of water as a medium for SMC in homogeneous and heterogeneous systems. This review covers the period from 2011 up to August 2015. Current challenges of palladium catalysed SMC in water include a) the reactivity with low-cost aryl chlorides, b) low catalyst loading, c) the functional group tolerance and d) mild reaction conditions. To address these challenges, several groups developed palladium-catalysed SMC in water with either homogenous- or heterogeneous systems.

2 Homogeneous SMC in Water

2.1 *P*-donors Ligands

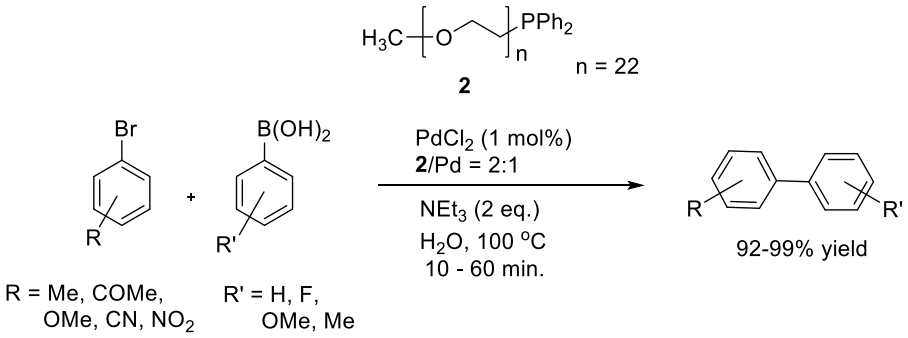
Because of the undesired decomposition of *P*-donors ligands, their use for aqueous SMC has remained limited compared to *N*-donor and NHC ligands. A handful example are found in the recent literature.

For example, Yu and co-workers reported SMC in water catalyzed by a supramolecular assembly held together with noncovalent interactions in the presence of palladium (Scheme 1).[16] For this purpose, they designed the tridentate ligand Phenylphosphinacalix[3]trifuran **1**. In the presence of palladium acetate, the resulting catalyst proved extremely active with turnover numbers as high as 3.05×10^{7} with 2×10^{-8} mol% Pd loading. The author suggested that these high TONs are not due to a facilitated oxidative addition step but the longevity of the catalyst may be a key to reach high TONs.

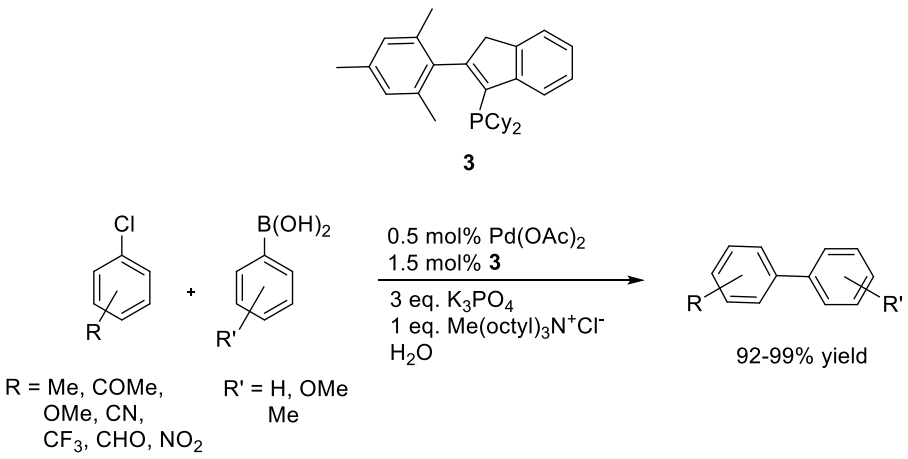


Scheme 1 Phenylphosphinacalix[3]trifuran **1** as an efficient ligand for the SMC in water.[16]

An efficient and recyclable protocol for the SMC in water was reported by Liu *et al*. based on the cloud point (Cp) of the thermoregulated ligand **2** (Scheme 2).[17] The palladium catalyst remains in the aqueous phase at lower temperature (< Cp, 93°C) but transfers into the substrate phase at higher temperature (> Cp, 93°C). This method allowed the preparation of a variety of biaryls in high yields (up to 99%) with 0.05 mol% Pd loading. The catalytic system can be recycled four times with high efficiency.



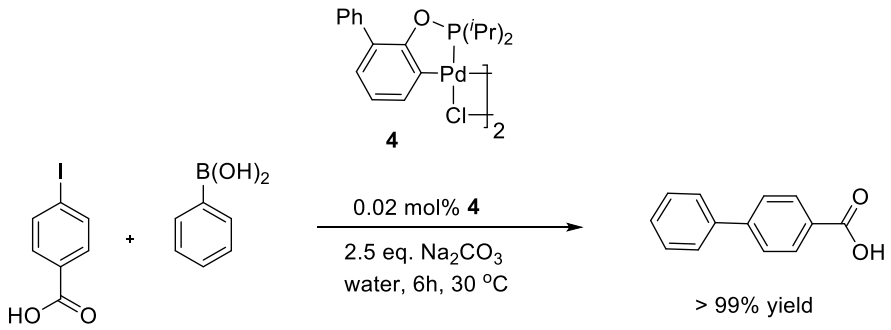
Scheme 2 A thermoregulated catalytic system for the SMC in water.[17]



Scheme 3 Bulky monophosphine ligand for the SMC in water developed by Liu and co-workers.[18]

Recently, Liu and co-workers[18] reported a catalytic system consisting of the (2-mesitylindenyl)dicyclohexylphosphine ligand **3** in combination with $[Pd(OAc)_2]$ and $[Me(octyl)_3N]^+Cl^-$ as the phase-transfer reagent. The resulting systems displayed high catalytic activity in the SMC of various aryl- and heteroaryl chlorides in water (Scheme 3).

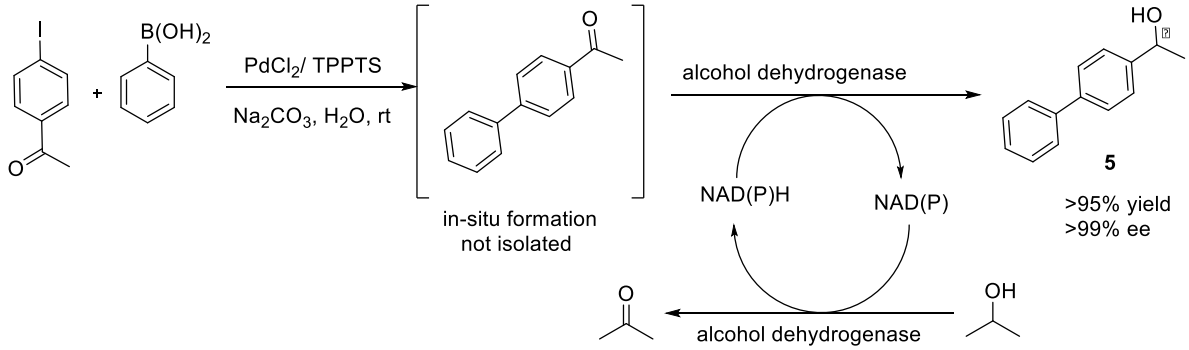
More recently, Eppinger and co-workers used the palladacycle **4**, under air and at room temperature, for the coupling of aryl iodides and bromides with a variety of boronic acids.[19] The biaryl products were obtained in excellent yields (up to 99%) with 0.02 mol% catalyst loading (Scheme 4). Poisoning experiments support the hypothesis of the homogenous nature of the catalytically active species, although the pre-catalyst **4** is insoluble in water.



Scheme 4 Palladacycle **4** for SMC in water developed by Eppinger and co-workers.[19]

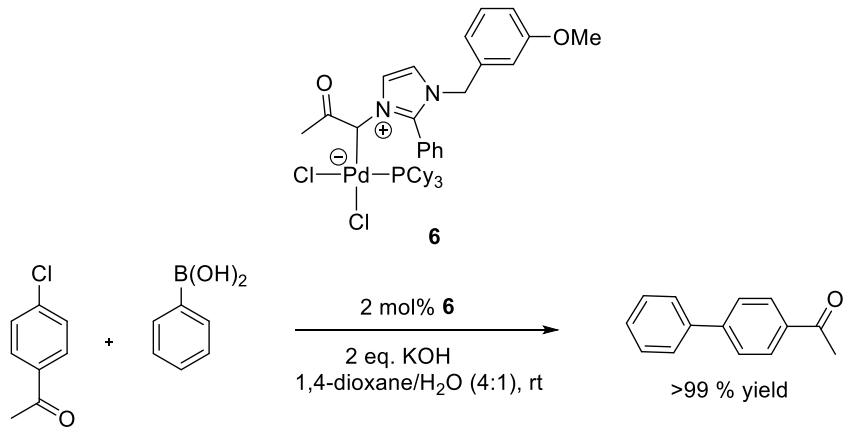
Later Gröger and co-workers reported the combination of a palladium-catalyzed SMC in aqueous medium with an enzymatic reduction in a one-pot process at room temperature.[20, 21] For the SMC, a water-soluble palladium catalyst was prepared from palladium chloride and TPPTS (TPPTS = tris(3-sulfonatophenyl)phosphine

hydrate, sodium salt). After completion of the reaction and adjustment of the pH to 7.0, the biaryl ketone product was reduced *in situ* via alcohol dehydrogenase (ADH). The desired biarylalcohol **5** was produced in up to >95% conversion (over the two steps) and excellent enantioselectivities (>99% ee) (Scheme 5).



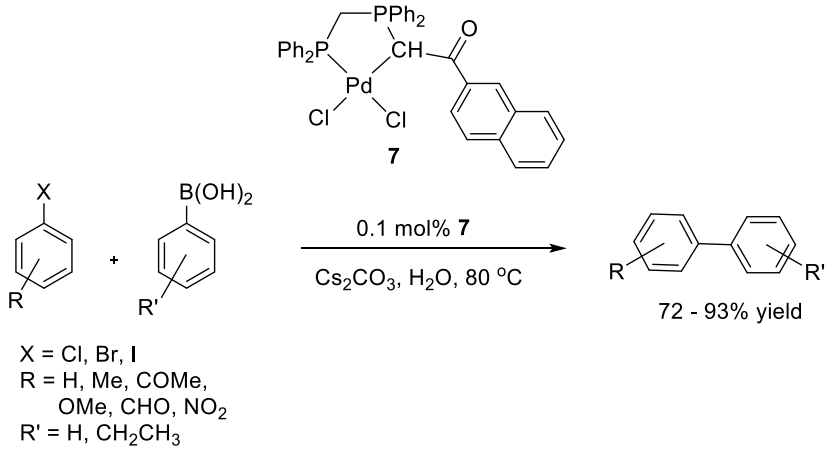
Scheme 5 SMC and subsequent enzymatic reduction for the synthesis of chiral biarylalcohols in water.[20]

In an independent study, zwitterionic palladium complexes were reported by Lee and co-workers for the SMC in water.[22] The zwitterionic phosphine complex **6** was efficient in catalyzing the SMC of sterically hindered aryl chlorides and arylboronic acids in dioxane/water (4:1) or neat water at room temperature (Scheme 6).



Scheme 6 A zwitterionic palladium **complexe 6** for the SMC in water.[22]

In a very recent study, Khazalpour and co-workers reported the palladium–phosphine system **7** as an active and recyclable pre-catalyst for SMC in water.[23] A five-membered chelate ring is formed upon coordination of the ligand through the phosphine and the ylidic carbon atom. The catalytic system could be reused four times without significant loss of activity (Scheme 7).



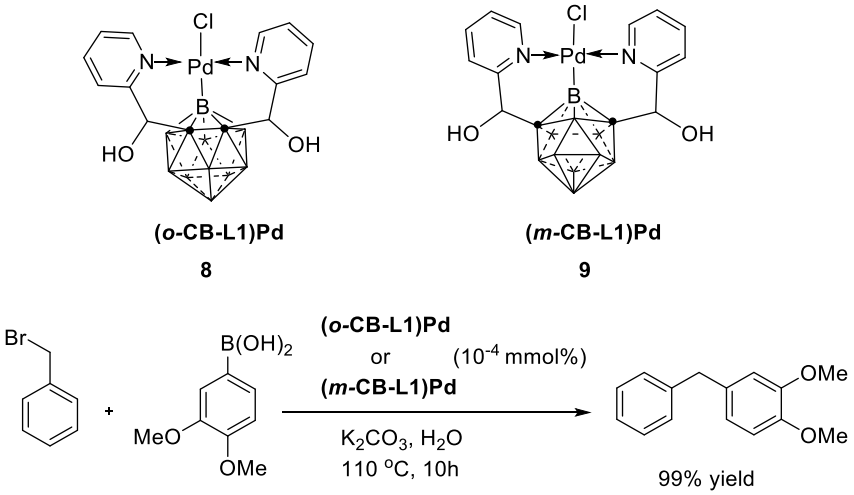
Scheme 7 A palladium–phosphine catalytic system **7** for SMC in water developed by Khazalpour and co-workers.[23]

2.2 *N*-donor Ligands

Although *N*-donor ligands have been widely neglected in homogeneous organometallic catalysis,[24] there has been a resurgence of interest for *N*-donor ligands in SMC. Various types of *N*-donor ligands are presented below: i) pyridines/imines, ii) imidates iii) pyrimidines iv) amines v) orthometallated palladacycles vi) amides and vii) hydrazones.

i) Pyridines/imines:

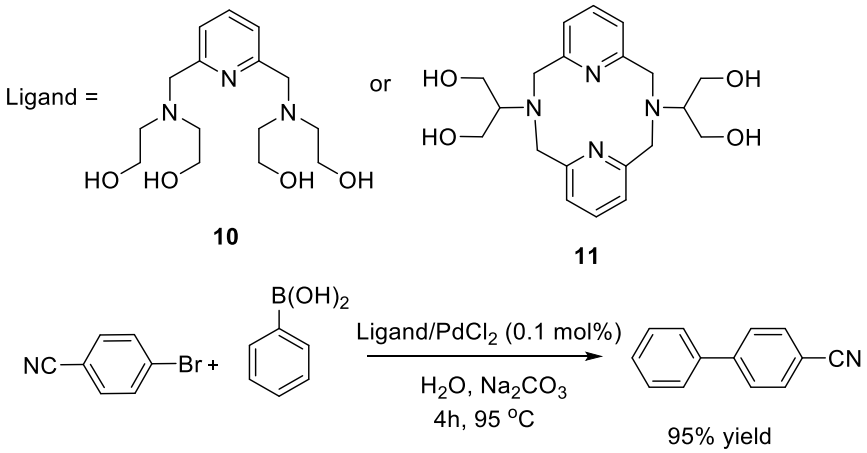
Planas and co-workers developed *o*- and *m*-carborane-based NBN pincer palladium complexes for SMC in water. These catalyst require remarkably low catalyst loadings (10^{-4} mmol %) and display good functional group tolerance.[25] They used an NBN pincer complex instead of an NCN pincer complex because of the stronger electron donating ability of the boron moiety which exhibited stronger *trans*-influence. Complex **(*o*-CB-L1)Pd 8** displayed a better catalytic profile than **(*m*-CB-L1)Pd 9** and with excellent conversions and TON values ranging from 770'000 to 990'000 (Scheme 8). Although potentially chiral, no mention is made on whether the ligands were used as a racemate, in their *meso*-form or in enantiopure form.



Scheme 8 SMC in water with *o*- and *m*-carborane-based NBN pincer palladium complexes.[25]

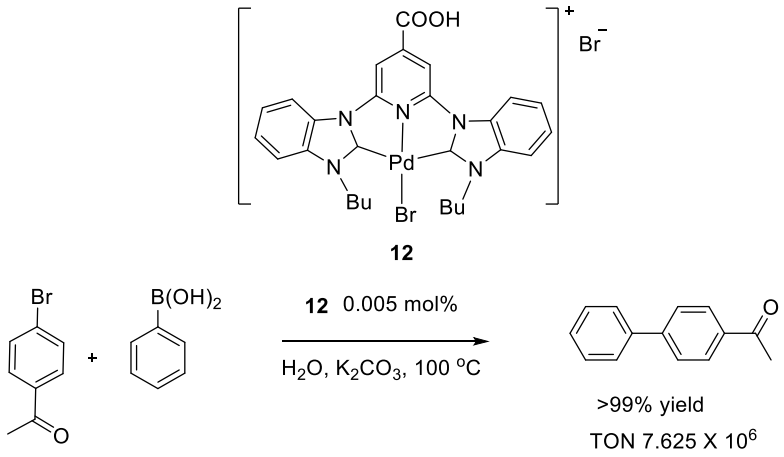
A set of water soluble pincer pyridine-diamine ligands **10**, **11** was developed by the Morales group for the SMC (Scheme 9). The presence of hydroxy-groups on the ligand ensures water solubility. Excellent yields were achieved (950 TON) for the

formation of biphenyls at 95°C in pure water.[26] Purification is readily achieved by decantation as the product is insoluble in water. The easy synthesis of the ligand from commercial starting materials, combined with the high catalytic activity of the corresponding complex deserves particular mention.



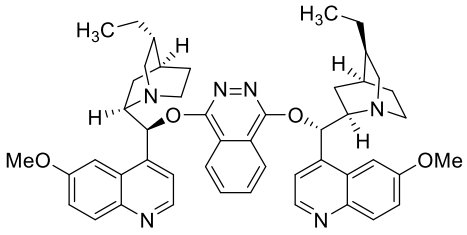
Scheme 9 SMC in water with water soluble pincer palladium complexes derived from ligand **10** or **11**.[26]

Recently, Tu and co-workers reported a hydrophilic pyridine-bridged bis-benzimidazolylidene palladium pincer complex **12** which is a highly efficient catalyst towards the SMC in water (Scheme 10).[27]



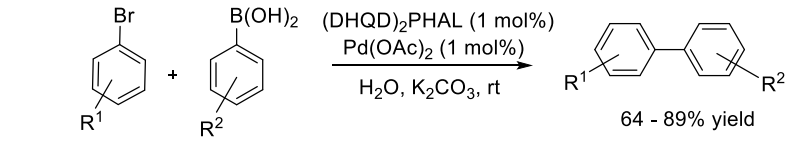
Scheme 10 Palladium-pincer complex **12** for the SMC in water.[27]

The $Pd(OAc)_2$–$(DHQD)_2PHAL$ **13** catalyzed SMC was reported by Saikia and co-workers (Scheme 11). This is a very simple, mild and efficient protocol for the synthesis of biaryls/heterobiaryls in neat H_2O at room temperature. Furthermore, the catalyst system is recyclable and can be employed in several consecutive runs without significant loss in catalytic activity.[28] No mention was made concerning the enantioselective SMC with this system.



13

$(DHQD)_2PHAL$

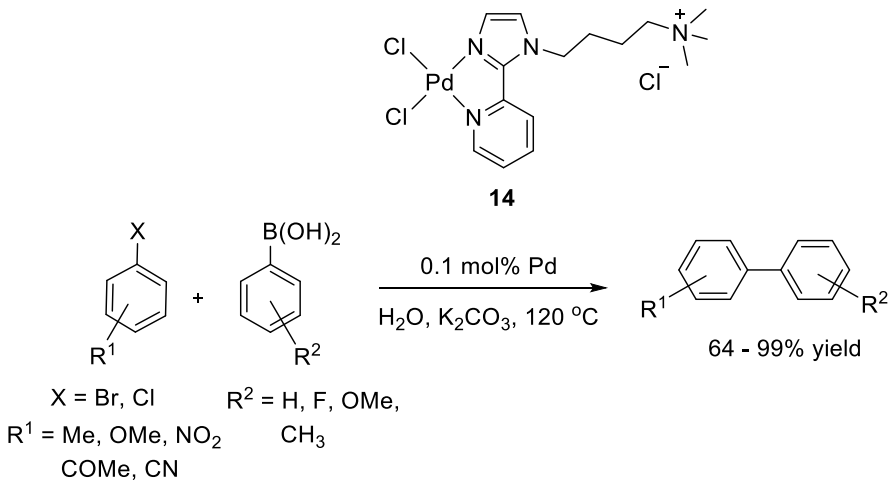


R^1 = Me, OMe, NO_2, CHO, COMe, CN, H R^2 = H, OMe, COMe, NO_2

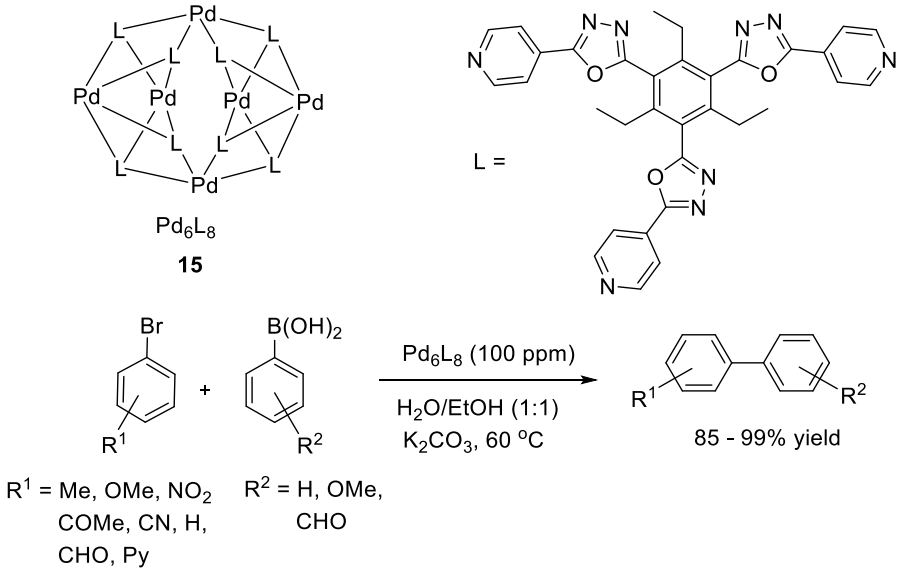
Scheme 11 $Pd(OAc)_2$–$(DHQD)_2PHAL$ **13** catalyzed SMC in water.[28]

$(DHQD)_2PHAL$ = Hydroquinidine 1,4-phthalazinediyl diether.

Wang and coworkers reported the synthesis of the palladium chelating complex **14** and its application for the SMC in air and water (Scheme 12).[29] The biaryl products were obtained in good to excellent yields with 0.1 mol% catalyst loading.



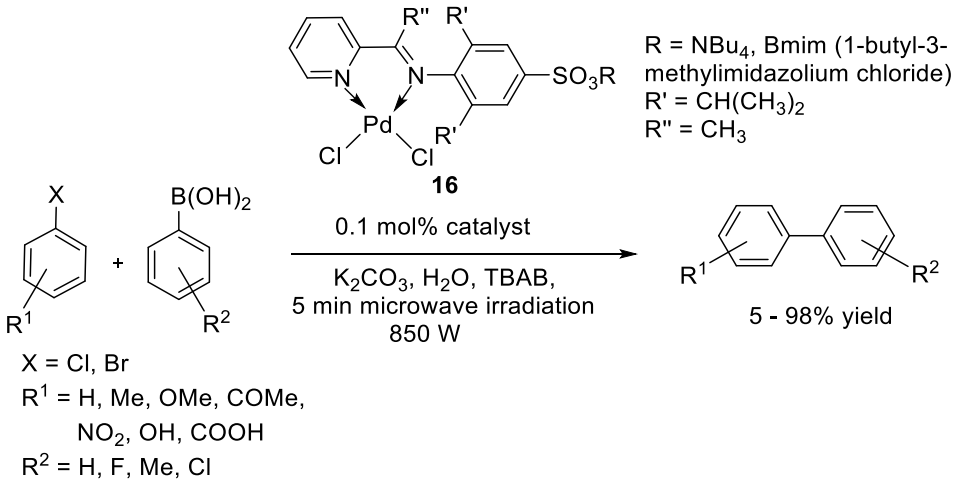
Scheme 12 Palladium chelating complex **14** for SMC in water developed by Wang and coworkers.[29]



Scheme 13 A self-assembled Pd_6L_8 cluster **15** for the SMC in water developed by Dong.[30]

A self-assembled hexanuclear cluster Pd_6L_8 **15** (L = 1,3,5-tris(4'-pyrirdyloxadiazol)-2,4,6-triethylbenzene) was reported by Dong for the SMC at very low catalyst loadings (i.e.100 ppm) (Scheme 13).[30] Depending on the solvent used for the SMC, the system was either homogeneous or heterogeneous: the reaction was homogeneous in water-ethanol whereas it was heterogeous in xylene.

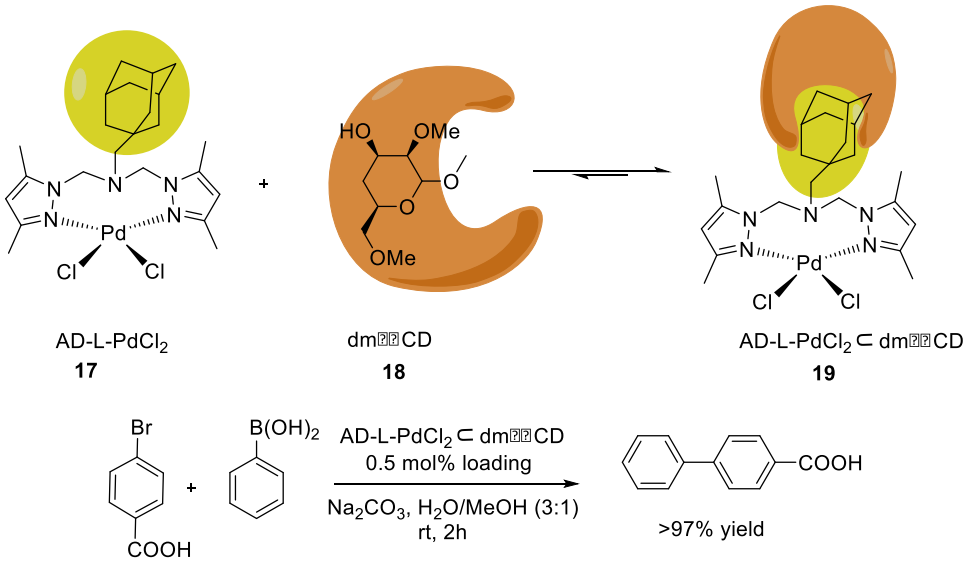
Senemoglu reported a microwave-assisted aqueous SMC catalyzed by unsymmetrical sulfonated water-soluble Pd(II)-pyridylimine complexes **16** (Scheme 14).[31] The compounds proved to be effective catalysts with up to 980 TON.



Scheme 14 Unsymmetrical sulfonated water-soluble Pd(II)-pyridyl imine complexes for SMC in water.[31]

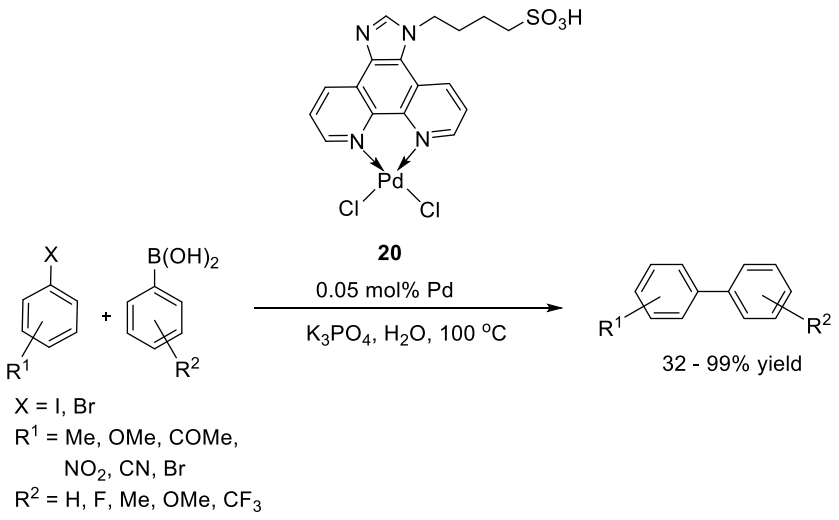
Recently, Hor and Young reported a supramolecular recyclable catalyst for the aqueous SMC (Scheme 15).[32] Upon host–guest incorporation of **17** within heptakis(2,6-di-*O*-methyl)-β-CD **18** in aqueous media, a water soluble supramolecular

assembly **19** was generated. This catalyst **19** (0.5 mol%) efficiently catalyzed the SMC (>97% yield) between hydrophilic aryl bromides with aryl boronic acid at room temperature.



Scheme 15 Supramolecular catalyst for aqueous SMC developed by Hor and Young.[32]

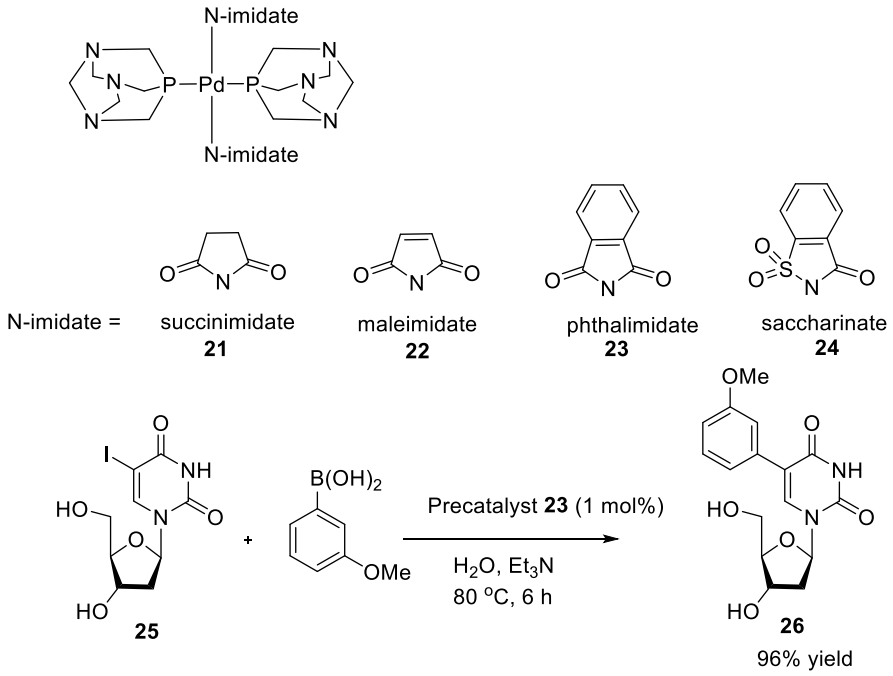
Lang and Li reported a $PdCl_2$/sulfonate-tagged phenanthroline precatalyst **20** for the SMC at 100°C in water (Scheme 16).[33] The cross-coupling products were obtained in good to excellent yields (TON upto 1980).



Scheme 16 Sulfonate-tagged phenanthroline palladium precatalyst for SMC in water.[33]

ii) Imidates:

Water-soluble palladium(II) complexes *trans*-[Pd(imidate)$_2$(PTA)$_2$] (imidate = succinimidate (suc) **21**, maleimidate (mal) **22**, phthalimidate (phthal) **23** or saccharinate (sacc) **24**) have shown to efficiently catalyze SMC of synthetically challenging substrates. The antiviral nucleoside analogue 5-iodo-2'-deoxyuridine **25** was used as substrate for the formation of the corresponding biaryl **26** in water under mild conditions (TON = 96).[34] Upon increasing the reaction time (48 hours), lower catalyst loadings (0.1 mol %) could also be used, without any appreciable erosion of the yield (Scheme 17).



Scheme 17 Imidate as ligands for the SMC of 5-iodo-2'-deoxycytidine developed by Serrano and co-workers.[34]

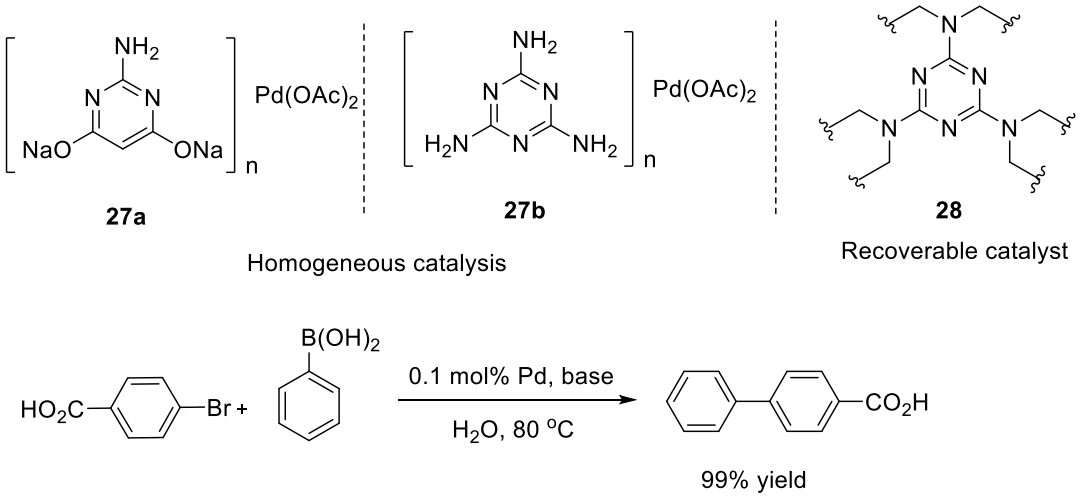
iii) Pyrimidines:

Prof. B. Davis reported an active pyrimidine ligand **27a** in 2009 for the aqueous SMC.[35] Inspired by this work, Chalker and coworkers[36] developed a melamine-palladium catalyst **27b** for the SMC in water (Scheme 18). The advantages of the melamine ligand over pyrimidine ligands are as follows:

i) It is less expensive than the pyrimidine.

ii) It is soluble in both water and organic solvents.

iii) The melamine-palladium catalyst can be cross-linked by reaction with formaldehyde to generate an insoluble polymeric catalyst **28** that can be recovered after the cross-coupling.

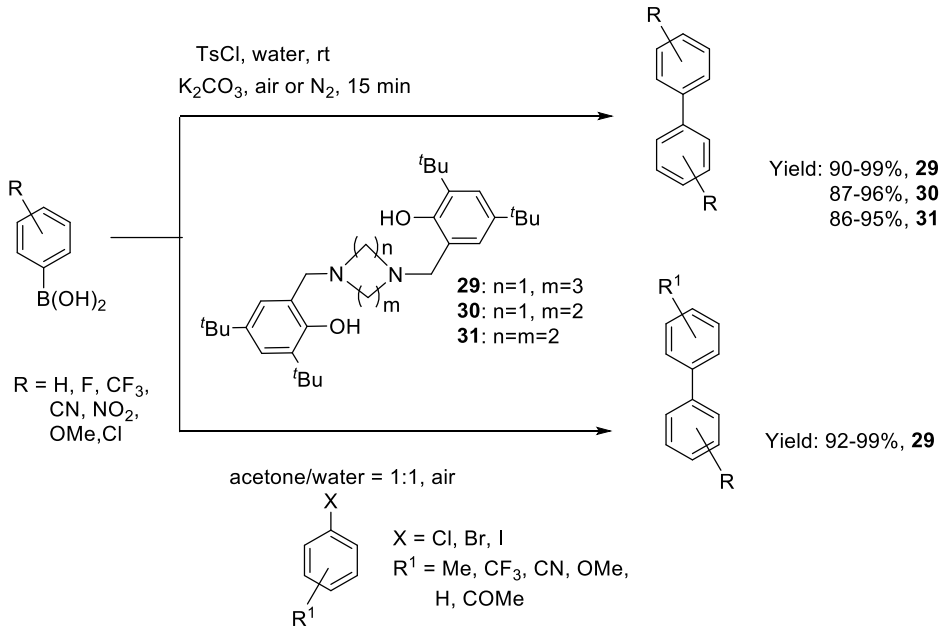


Scheme 18 Davis' ligand **27a** for aqueous SMC. Crosslinked and related insoluble melamine-palladium catalysts for the SMC in water developed by Chalker and coworkers.[36]

iv) Amines:

Zhou and coworkers[37] investigated the influence of the chelate ring size (i.e. 5 or 6), and the relative position of both *N*-donors and bulkiness of *N*-aryl substituents in amine-bridged bis(phenol) ligands (**29**, **30** and **31**) on the palladium-catalyzed SMC (Scheme 19). The homocoupling of arylboronic acid could be completed in neat water with the aid of a catalytic amount of *p*-toluenesulfonyl chloride (TsCl) in a very short time under anaerobic or aerobic conditions. Interestingly, the same catalytic system

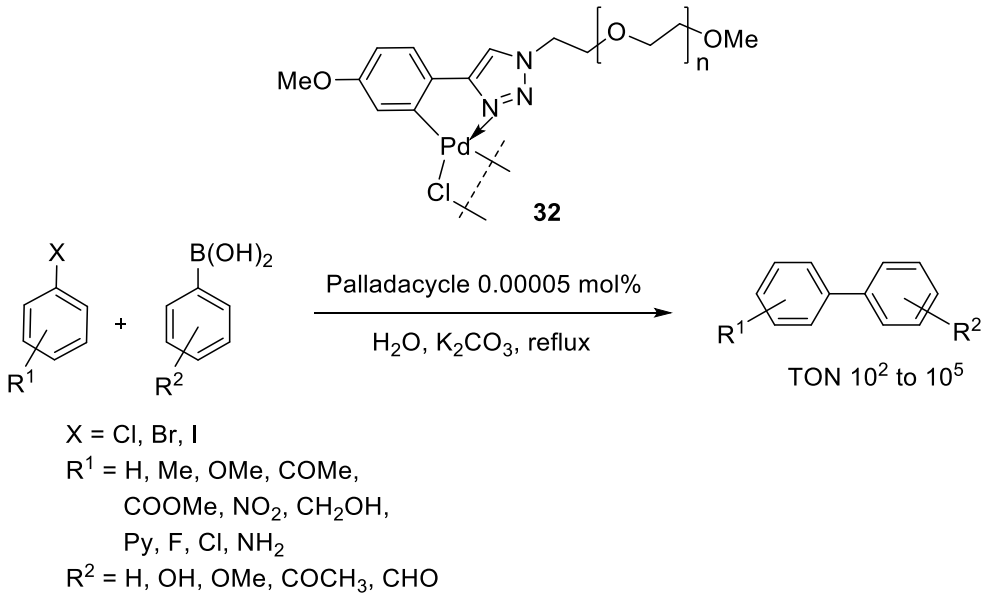
was efficient for the SMC in aqueous acetone under aerobic conditions in the absence of TsCl.



Scheme 19 Amine-bridged bis(phenol) ligands for the aqueous C-C cross-coupling reactions.[37]

v) Orthometallated palladacycles:

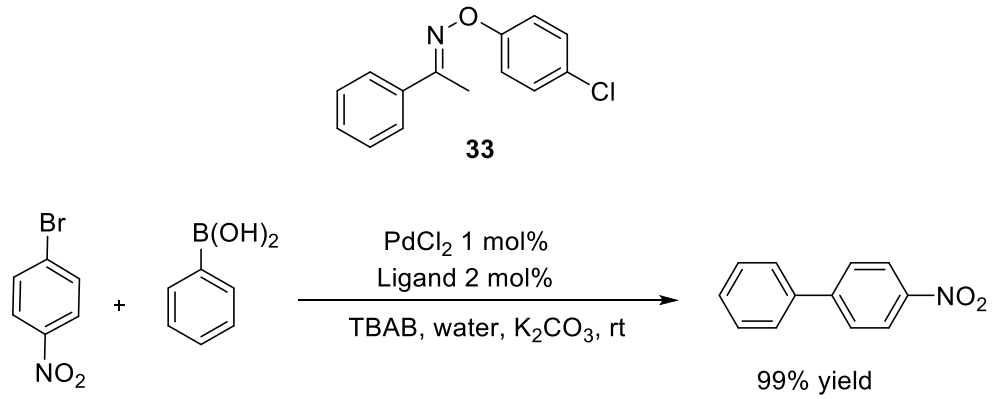
Palladacycles are interesting because they are believed to release highly active Pd(0) species at a very slow rate, which prevents the deactivation of Pd(0) such as nanoparticle formation, thus achieving high turnover numbers. Palladacycles are



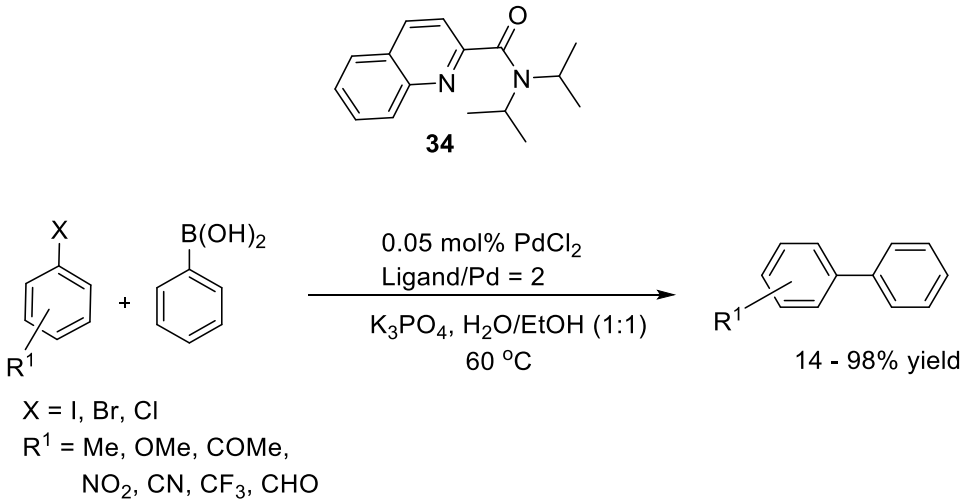
Scheme 20 SMC in water with an orthometallated aryltriazole palladium complex bearing a PEG solubilizing unit.[38]

formed by C-H activation of aromatic moiety near a coordination site in the ligand. A novel water-soluble palladacycle **32** has been reported by Ding (Scheme 20).[38] The catalyst exhibited superior catalytic activity towards the SMC in neat water with TONs of up to 9.8×10^5. In addition, the catalyst could be reused at least 3 times without significant loss of activity.

Bora and coworkers studied *O*-Aryloxime ether analog **33** as ligands in the palladium-catalyzed SMC of aryl bromides and aryl boronic acids in water at room temperature.[39] The reaction conditions for the cross-coupling were optimized using $PdCl_2$ and $Pd(OAc)_2$ under aerobic conditions (Scheme 21). To the best of our knowledge, this is the only example of an oxime ether used as a ligand. The aryl ring of the aryloxime ether is believed to undergo orthometalation through C-H activation to form highly active palladacycle.



Scheme 21 *O*-Aryloxime ether as ligand in palladium-catalyzed SMC in water.[39]



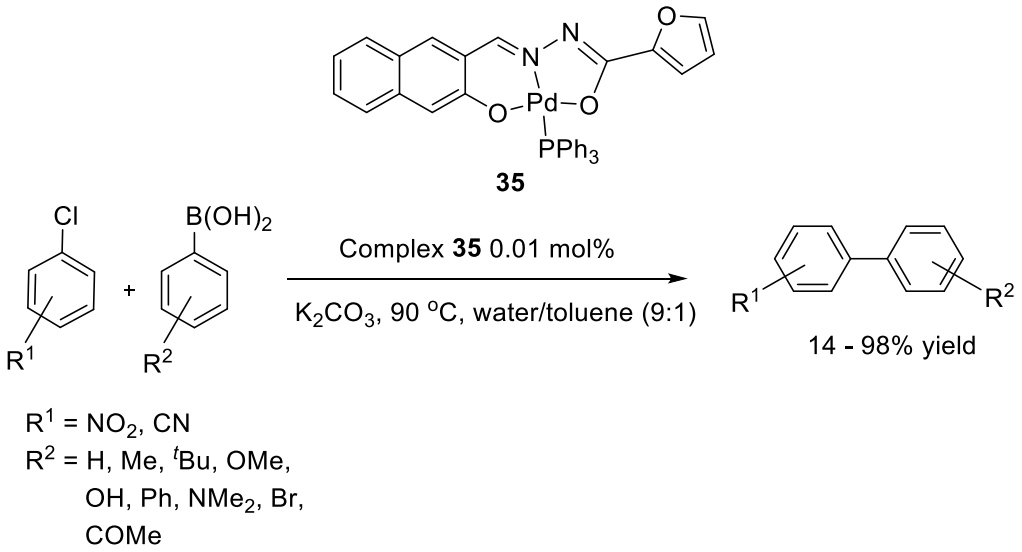
Scheme 22 Bidentate amide ligand based on a quinoline derivative used for the SMC in water.[40]

vi) Amides:

Jiang and Tan recently reported an SMC in water relying on the amide-bearing quinoline derivative **34** as a ligand.[40] With 0.05 mol% Pd loading, they obtained up to 98% yield at 60–90 °C under air (Scheme 22).

vii) Hydrazones:

Nallasamy and co-workers reported a palladium(II) complex **35** bearing a series of ONO tridentate heterocyclic hydrazone ligands for SMC of substituted aryl boronic acids with aryl chlorides in a water–toluene system (9 : 1).[41] The catalyst was highly active with 0.01 mol% loading to afford 99% yield of the coupled product (Scheme 23).

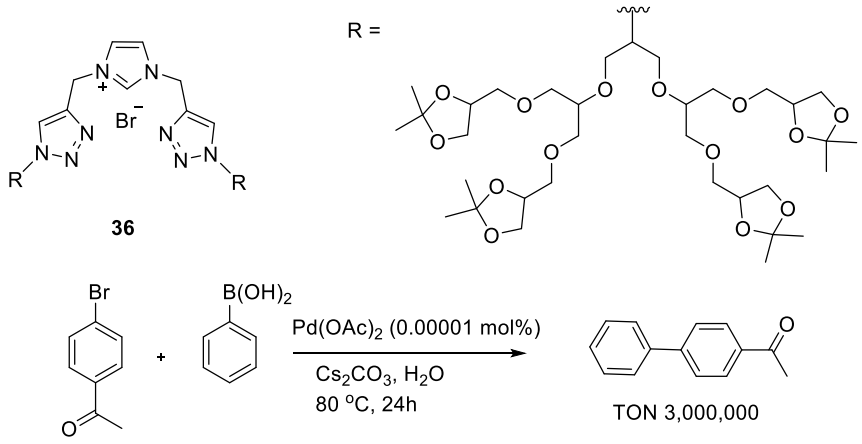


Scheme 23 Tridentate heterocyclic hydrazone ligand for SMC in water.[41]

2.3 *N*-heterocyclic Carbene (NHC) Ligands

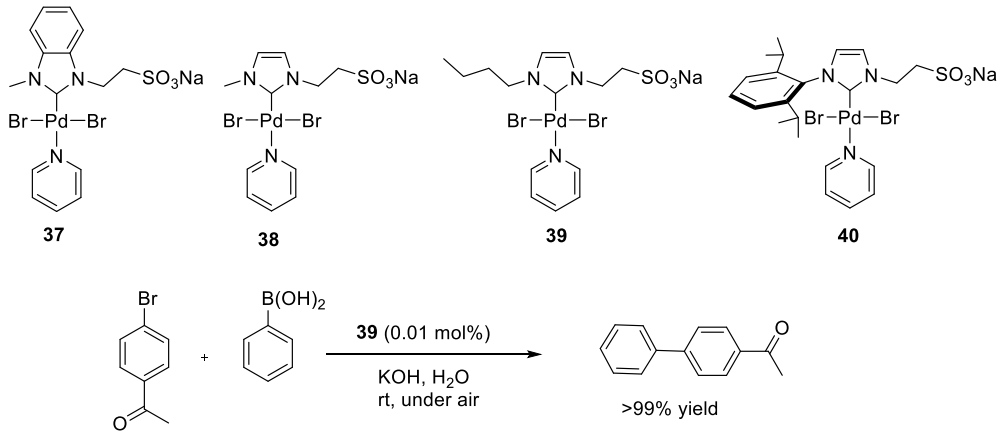
NHC ligands are strong electron-donors and can be sterically demanding. Recently, their use in aqueous media has received attention. The carbene donor-carbon of an NHC is strongly basic (pK_a about 20), which generally precludes their use as free ligands in aqueous media. thanks to the strong metal-NHC bond, metal complexes of water-soluble NHCs are often water soluble. The Haag group reported a highly active glycerol-dendron-supported *N*-heterocyclic carbene ligand **36** with $Pd(OAc)_2$ as a catalyst (Scheme 24). A symmetrical ligand structure was designed to provide a

larger micro-environment with the catalytic site at the core position. Deprotection of the dendritic-supported catalysts allowed to perform the catalytic reaction in neat water.[42]



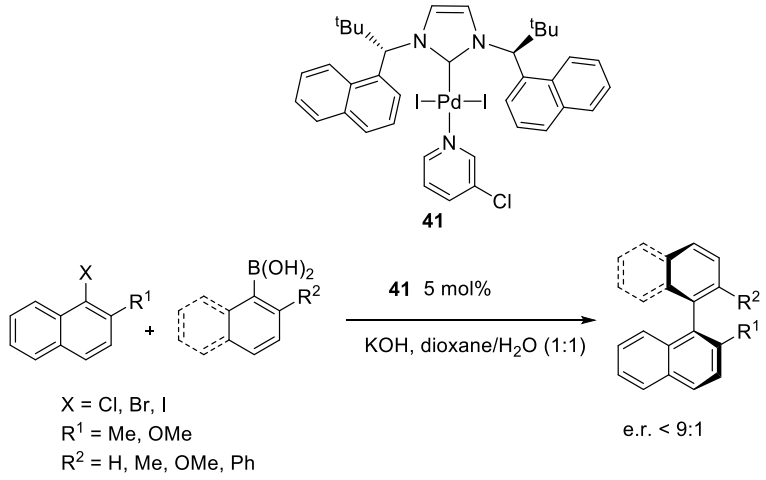
Scheme 24 Dendritic supported NHC-palladium catalysts for SMC with a L/Pd Ratio of 1.1:1.

Four water-soluble PEPPSI-type (pyridine, enhanced, precatalyst, preparation, stabilization and initiation) Pd-NHC complexes (**37–40**) were developed by Kühn and Pöthig for the SMC in water under air (Scheme 25).[43] Complex **37**, bearing a 2,6-diisopropylphenyl substituent, displayed the best catalytic activity for a variety of aryl bromides with a catalyst loading of 0.1 mol% even at room temperature. The catalyst can be used in at in least four consecutive runs without significant loss of activity.



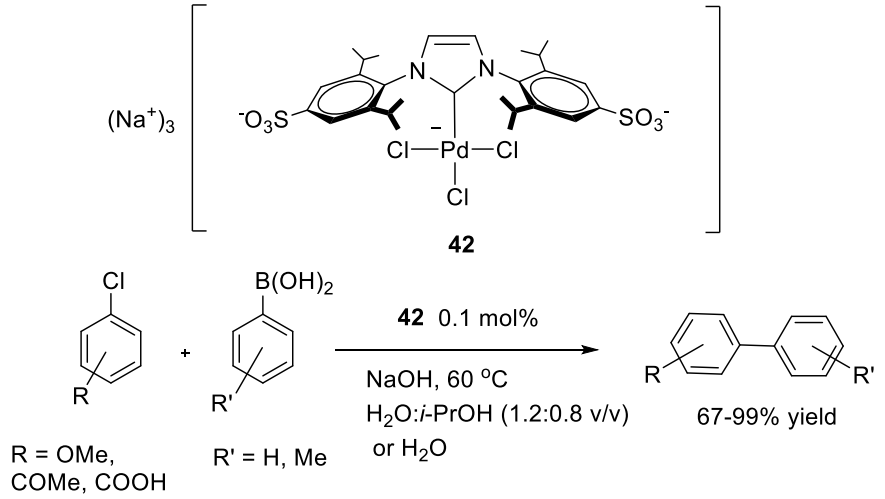
Scheme 25 Water-soluble PEPPSI-type -Pd-NHC complexes for aqueous SMC.[43] (PEPPSI = pyridine, enhanced, precatalyst, preparation, stabilization and initiation)

An asymmetric SMC using chiral PEPPSI complex **41** incorporating bulky enantiopure *N*-heterocyclic carbenes was developed by Kündig and coworkers.[44] They obtained up to 85% yield and 80% ee for coupling of 1-halo-2-methylnaphthalene with naphthylboronic acid. Unfortunately, the product was contaminated with an inseparable product resulting from homocoupling (Scheme 26).



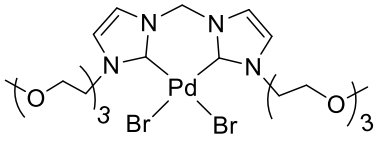
Scheme 26 Asymmetric SMC with chiral PEPPSI complexes incorporating bulky *N*-heterocyclic carbene ligands.[44]

Water-soluble Pd(II)(NHC) complexes **42** containing two sterically-hindered sulfonated groups have been prepared by Jesus.[45] These complexes are active catalysts for the SMC of aryl chlorides and boronic acids in mixtures of isopropyl alcohol/water or, in the case of water-soluble aryl chlorides, in pure water (Scheme 27). For some of the most hindered aryl chlorides, small amounts of monoarenes are formed via a competitive hydro-dehalogenation process.



Scheme 27 Synthesis of biphenyls by SMC catalyzed by palladium(II) complexes bearing sulfonated N-Heterocyclic Carbenes.[45]

Palladium complexes with chelating, oligo-ethylene glycol-substituted bis-NHC ligands have been prepared by Strassner.[46] The resulting Pd-complex **43** displays excellent water solubility and very high catalytic activity. Up to 80'000 TONs could be achieved in a 1 : 1 water methanol mixture at 100 °C (Scheme 28). The palladium complexes showed excellent solubility in water. Very high catalytic activity was achieved even at ppm catalyst loadings.



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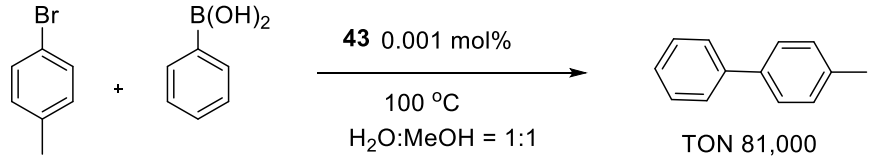
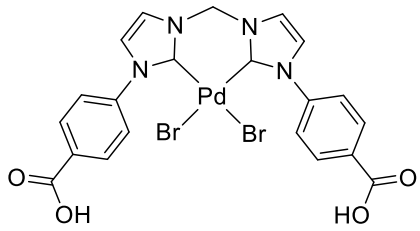


Scheme 28 Oligo ethylene glycol substituted bis-NHC ligands for SMC in a water-methanol mixture.[46]

A very similar complex **44** was also prepared by Wang and coworkers.[47] Deprotonation of carboxylic acid group rendered it water-soluble (Scheme 29).



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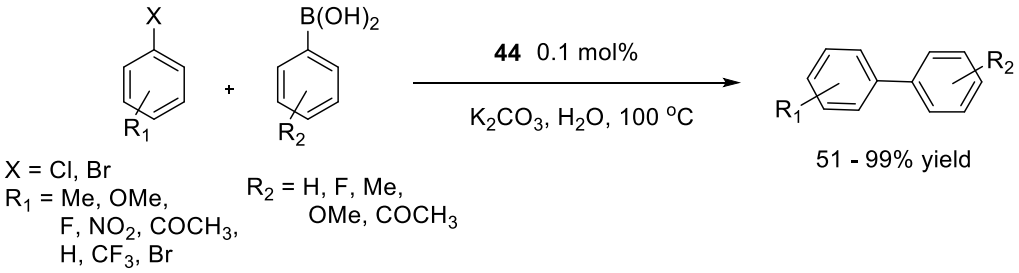
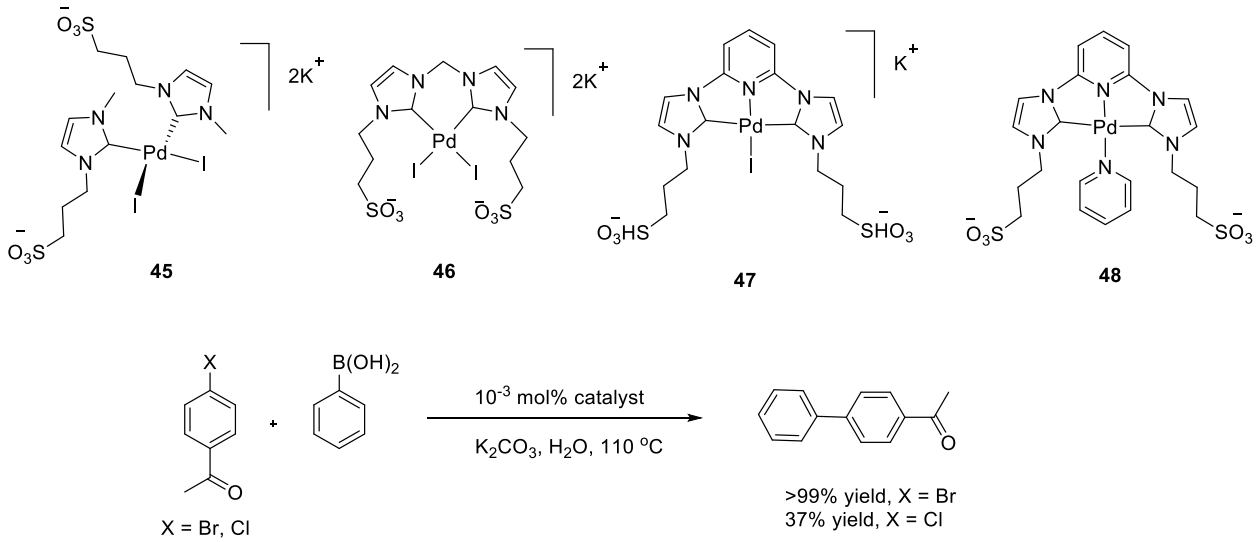


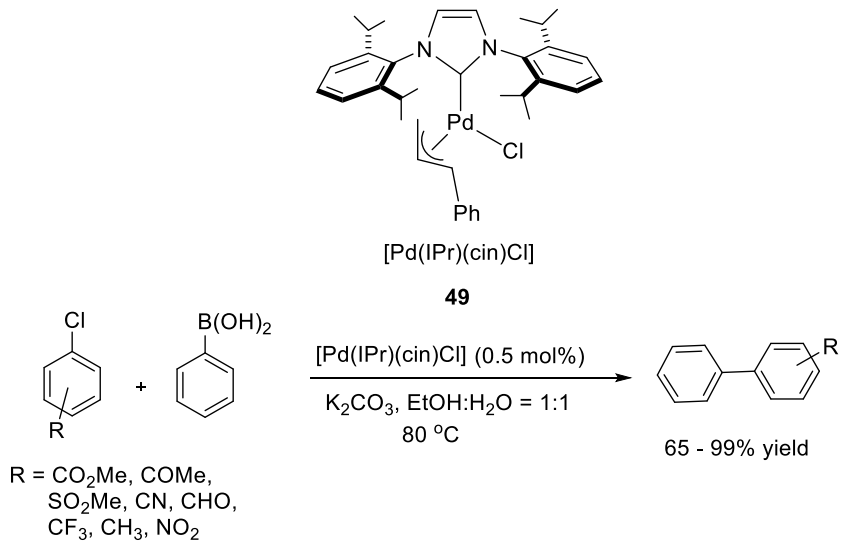
Scheme 29 Chelating-NHC-palladium complex for the SMC in water.[47]

In a study, Peris and Godoy compared four bis-NHC-palladium complexes **45** – **48** for the SMC in water.[48] The bis-NHC-palladium complex **45**, in which the two NHC ligands are in a relative cis configuration, afforded the best catalytic system, with

TONs > 10^5 for 4-bromoacetophenone and 3.7 × 10^4 for 4-chloroacetophenone (Scheme 30).



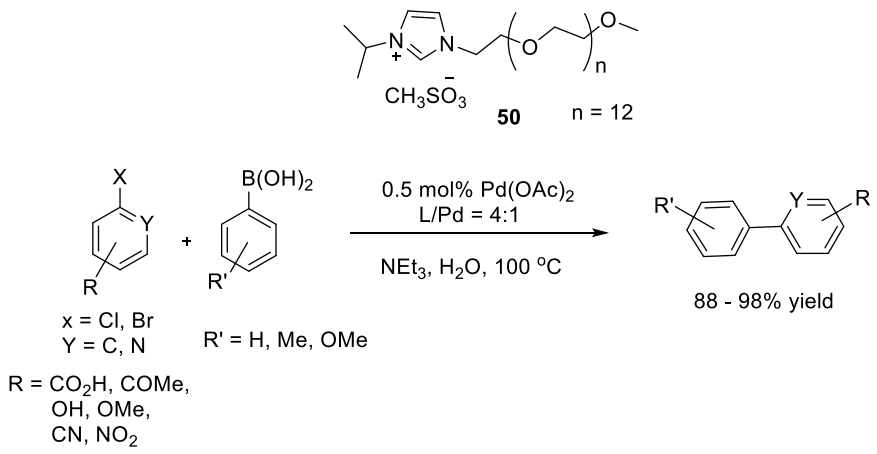
Scheme 30 Palladium catalysts with sulfonate-functionalized-NHC ligands for the SMC in water.[48]



Scheme 31 An SMC in water based on a commercially available precatalyst.[49]

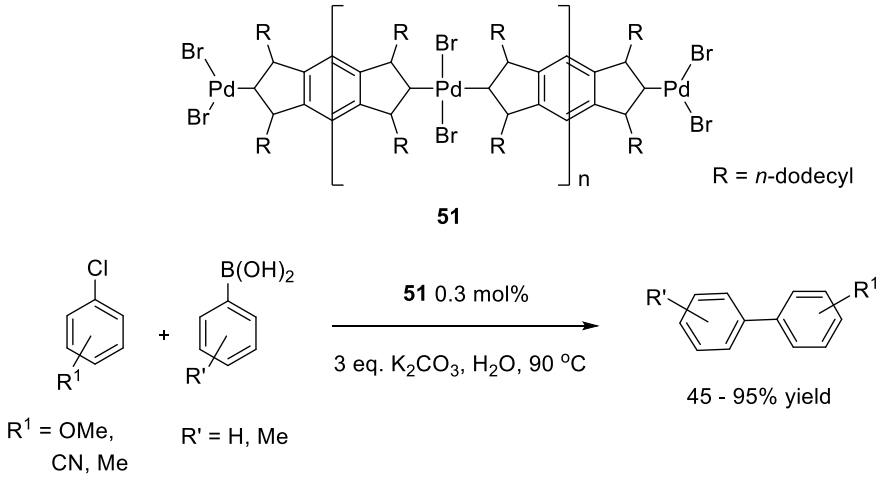
Nolan and coworkers recently reported the SMC using a Pd-NHC catalyst at low catalyst loading.[49] The commercially available and air-stable [Pd(IPr)(cin)Cl] pre-catalyst **49** led to the formation of various functionalized biaryls from aryl chlorides and boronic acids under very mild conditions using a mixture of ethanol/water as solvent and an inorganic base (Scheme 31).

Liu and coworkers[50] reported the synthesis of water-soluble imidazolium salts **50** bearing poly(ethyleneglycol) moieties directly attached to an *N*-atom of imidazole. The catalytic system generated in situ from a source of [$Pd(OAc)_2$], a precursor of imidazolium salt, and triethylamine catalyzes the SMC in water (Scheme 32).



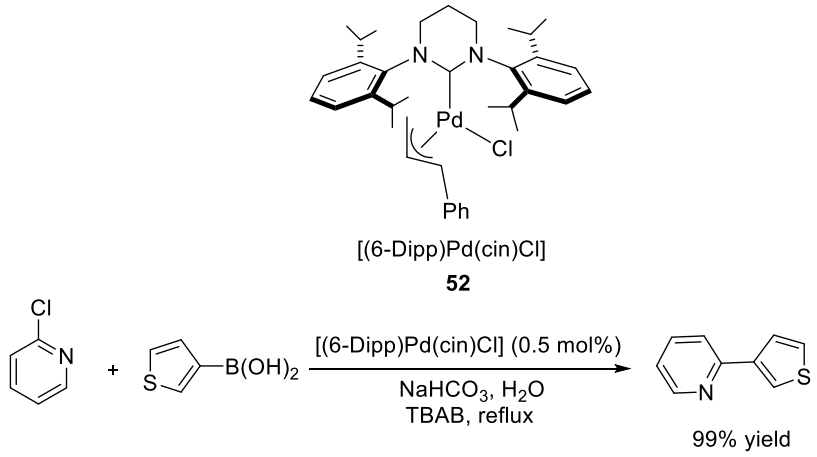
Scheme 32 Poly(ethylene glycol)-functionalized imidazolium salts–palladium-catalyzed SMC in water.[50]

Karimi and coworkers showed that Pd-NHC polymers **51** can be used as catalyst for SMC in water (Scheme 33).[51, 52] Although the mechanism is not clear, this polymer showed very high activity for the coupling of aryl chlorides, together with excellent recyclability.



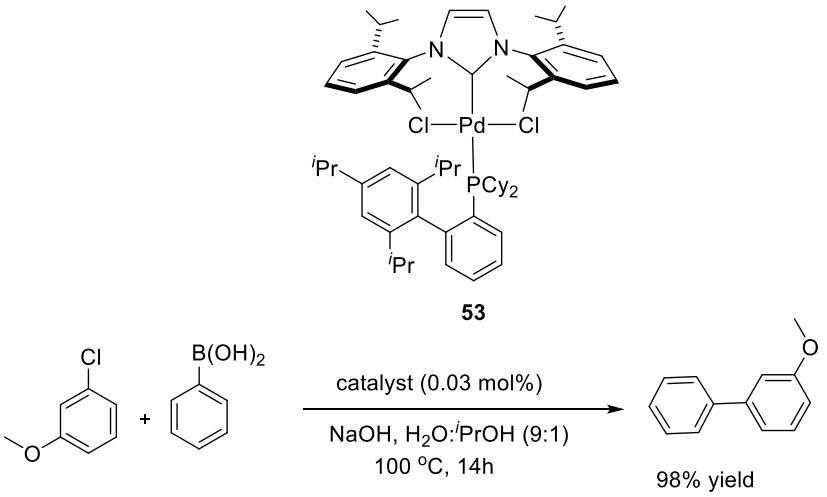
Scheme 33 Pd-NHC oligomers for aqueous SMC developed by Karimi.[51]

Recently, Nechaev and co-workers synthesized the six-membered ring NHC containing complex **52**, which was used for the cross-coupling of heteroaryl bromides and chlorides with heterocyclic boronic acids in water (Scheme 34).[53] The cross-coupled products were obtained in very good yield with 0.5 mol% catalyst loading (TON up to 200).

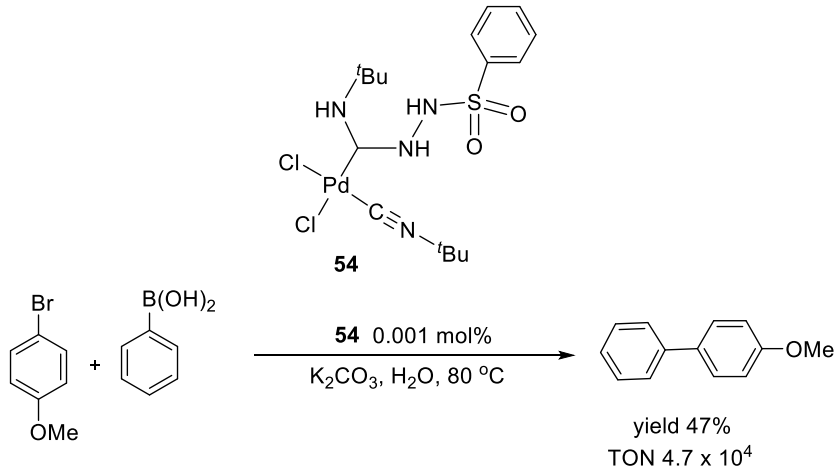


Scheme 34 Expanded ring NHC palladium **complex 52** for the SMC in water.[53]

The same year Cazin and co-workers reported on the synthesis of a mixed PR_2Ar /NHC Pd complex **53** that was used in SMC of aryl chlorides using very low catalysts loadings in aqueous solutions (water/isopropanol 9:1) (Scheme 35).[54]



Scheme 35 Mixed phosphine/N-heterocyclic carbene palladium complexes for SMC in water.[54]



Scheme 36 Acyclic diaminocarbene (ADC) palladium **complex 54** for SMC in water.[55]

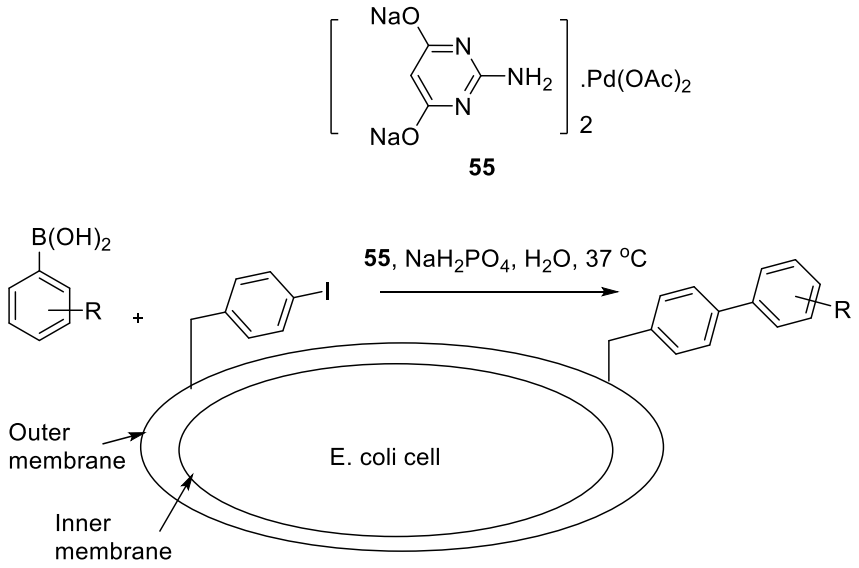
In an alternative strategy relying on acyclic carbene ligands, Boyarskiy and Luzyanin[55] reported palladium complexes with acyclic diaminocarbenes [Pd-(ADCs)] (Scheme 36). The catalyst **54** efficiently catalyzed the SMC of organohalides with a range of aryl boronic acids at 80°C within 2h (100°C and 3 h for the chlorides). Biaryls were obtained in yields up to 99% and with maximum TONs of 9.9×10^3 (for aryl iodides), 4.7×10^4 (for aryl bromides), and 9.2×10^3 (for aryl chlorides).

2.4 Homogeneous SMC for Chemical Biology Applications

More recently, the SMC has found applications in the context of chemical biology. Indeed, both reactants (i.e. arylhalides and boronic acids) and products (i.e. biaryls) can be regarded as bio-orthogonal.[35, 56–61] In this context however, high catalyst loadings are routinely required for reactions performed in a biological environment.[35, 56, 57, 60, 62–70] Ueno and coworkers anchored a palladium moiety within a ferritin container to yield an artificial metalloenzyme. The resulting artificial metalloenzyme however did not outperform the free cofactor (no enantioselectivity, turnover frequency: 3500 h^{-1}).[57]

The Davis group reported a convenient catalyst for the SMC using a modified protein as substrate.[35, 59, 71, 72] An effective ADHP (2-amino-4,6-dihydroxypyrimidine)-based catalyst system $[Pd(OAc)_2(ADHP)_2]$ **55** was gave full conversion (>95% yield, 95 TON) between a protein bearing aryl iodide moiety and a broad range of aryl-/vinyl-boronic acids.[63] Recently, in a continuous effort to apply transition-metal-mediated reactions in living systems, the Davis' group demonstrated the first application of the SMC on the outer-membrane protein OmpC of *Escherichia coli*

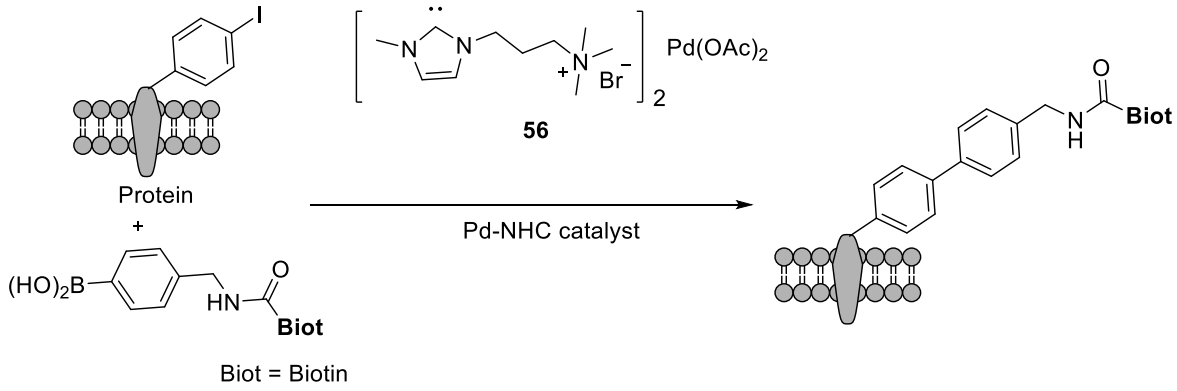
cells.[60] Here, a bacterial surface protein, OmpC was engineered by incorporation of 4-iodo-phenylalanine (Scheme 37). A reaction in the presence of a fluorescent boronic acid as coupling partner, catalyzed by $[Pd(OAc)_2(ADHP)_2]$ (200 mol%), afforded the fluorescent cross-coupled product, anchored on the bacterial surface. The ADHP-based catalysts showed excellent labelling efficiency and low cytotoxicity in bacteria cells, although the reaction was not catalytic..[73]



Scheme 37 (2-amino-4,6-dihydroxypyrimidine)-based catalyst system for SMC on the outer-membrane protein OmpC of *E. coli* developed by Davis group.[60]

Wang and Chen reported on a water-soluble *N*-heterocyclic carbene (NHC)-stabilized-palladium complex for the SMC of biomolecules under mild conditions in water (Scheme 38).[67] The Pd–NHC complex **56** bearing hydrophilic groups was an efficient catalyst for the SMC of various unnatural arylhalide-bearing amino acids (TON up to 95). The authors further exploited this catalytic system for the rapid

bioorthogonal labeling of proteins on the surface of mammalian cells. In this case, they used a stoichiometric amount of catalyst but there is no mention of yield or TON.



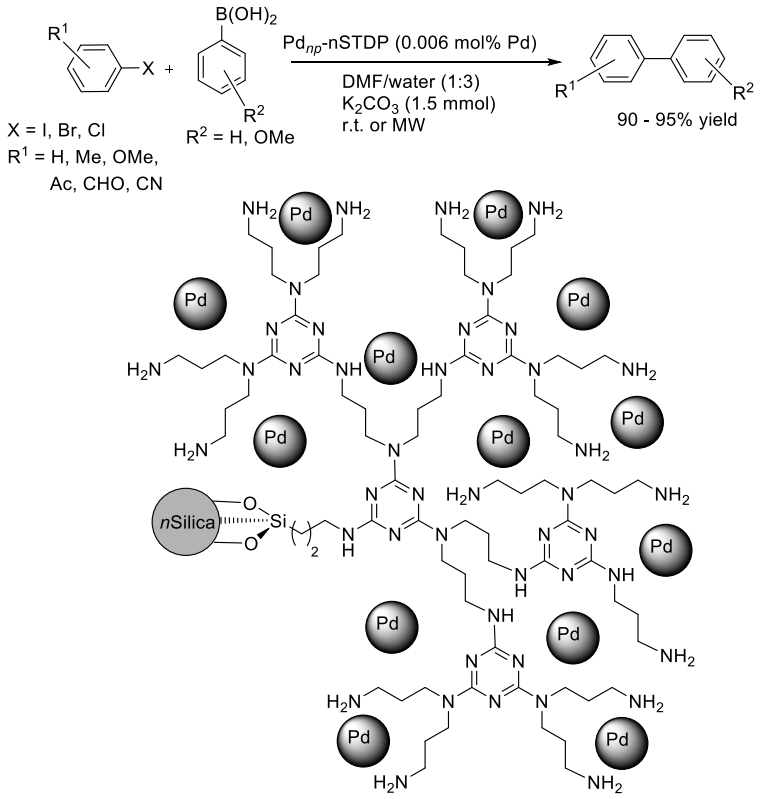
Scheme 38 Pd-NHC catalyzed SMC on a cellular system developed by Wang and Chen.[67]

3 Heterogeneous SMC in water

In view of the high cost and the shortage of palladium, its recovery and recycling is an important issue for any large scale application. Therefore, a variety of inorganic and organic solid-supported catalytic systems have been developed to address these challenges. In this context, heterogeneous Pd-catalysts are more attractive than the homogeneous Pd-catalysts as their recovery is facilitated. Residual palladium is a particular concern in the synthesis of pharmacophores, where very stringent precious metal restrictions apply. Unfortunately, compared to their homogeneous counterparts, solid-supported catalysts often suffer from lower activity and selectivity. It is thus highly desirable to develop highly efficient supported SMC catalysts.

3.1 Supported catalysts

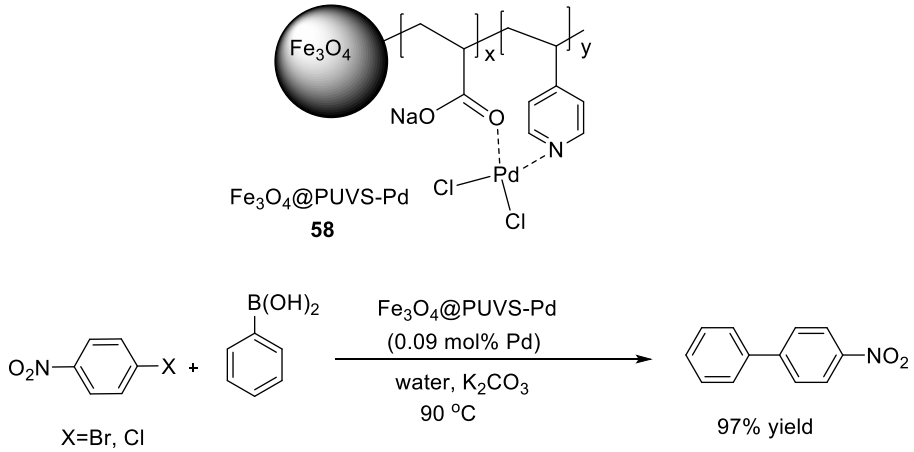
Polymer-modified nanoparticle-supported catalysts have generated a lot of interest due to their unique properties. Polymer supports can be chemically modified easily with functional groups to coordinate with transition metals, potentially improving the long-term stability of the catalyst. Moreover, the nanoparticles may enhance the catalytic performance thanks to their large surface-to-volume ratios and high densities of active sites relative to the bulk metals. Polymer-modified nanoparticles are expected to combine the advantages of both the homogeneous and heterogeneous catalysts.



Scheme 39 Palladium nanoparticles on a nano-silica triazine dendritic polymer as catalyst for aqueous SMC.[74]

Isfahani and colleagues[74] recently prepared a catalyst **57** by immobilizing palladium nanoparticles on a nano-silica triazine dendritic polymer. This catalyst exhibited high activity for the SMC even with 0.006 mol% palladium loading (Scheme 39). In addition, it could be reused six times with no apparent decrease in yield. The catalyst was recovered by centrifugation, which might be a limitation for large scale applications.

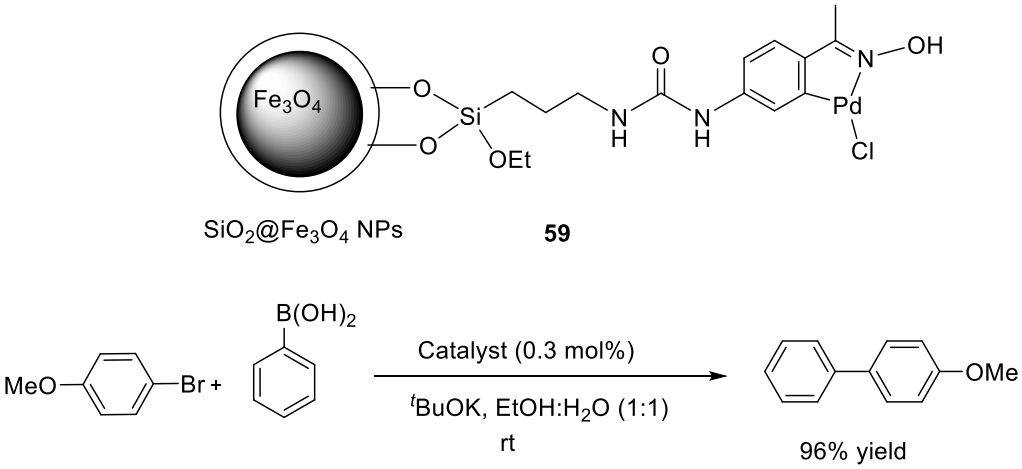
To circumvent the challenge associated with separation of catalyst from the reaction medium by filtration or centrifugation, magnetically-separable catalysts have attracted much attention recently. A magnetically responsive polymer nanocomposite Fe_3O_4@poly(undecylenic acid-*co*-4-vinyl pyridine-*co*-sodium acrylate) (PUVS) **58** was introduced by Bian.[75] This catalyst exhibited excellent catalytic activity for



Scheme 40 Magnetic polymer-nanocomposites as catalyst for SMC in water developed by Bian.[75] PUVS = poly(undecylenic acid-co-4-vinyl pyridine-co-sodium acrylate)

both Heck and SMC in water, and could be conveniently separated and recovered by applying a permanent magnet (Scheme 40). The supported catalyst could be used consecutively for six runs without significant loss of catalytic activity.

A novel magnetic nanoparticle-supported oxime palladacycle catalyst **59** was prepared and characterized by Gholinejad.[76] The magnetically recoverable catalyst was employed at room temperature for the SMC of aryl iodides and bromides in aqueous media. The catalyst was shown to be highly active under low Pd loading (0.3 mol%) (Scheme 41). The catalyst could be easily recovered from the reaction mixture using an external magnet and reused for six consecutive runs without significant loss of

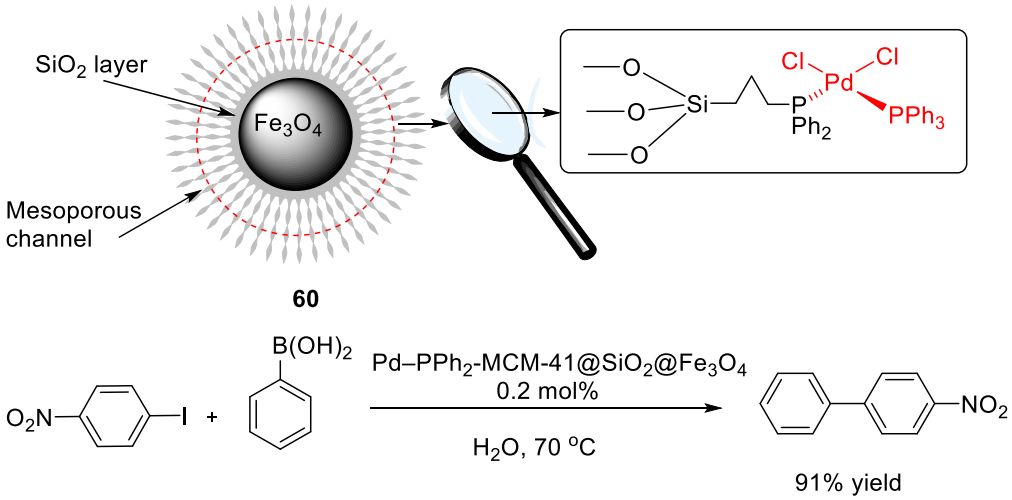


Scheme 41 Magnetic nanoparticle-supported oxime palladacycle catalyst for the SMC in water.[76]

activity. A similar kind magnetically-separable palladium catalyst was also developed by Karimi and co-workers relying on imidazolium ionic liquid bearing triethylene glycol moieties on the surface of silica-coated iron oxide nanoparticles.[77] The biaryl

products were obtained upto 95% yield with 0.25 - 0.50 mol% Pd loading under argon atmosphere.

Li and co-workers recently reported on a recyclable ordered mesoporous magnetic organometallic catalyst **60** for SMC in water (Scheme 42).[78] They immobilized the catalyst precursor onto undoped and functionalized ordered mesoporous silicas (MCM-41) coated on Fe_3O_4 magnetic microspheres. The catalytic efficiencies were comparable with those of the homogeneous catalysts, and they could be easily recycled (eight times) for reuse by applying an external magnet.



Scheme 42 Palladium complexes anchored to an MCM-41 thin layer coated on Fe_3O_4 microspheres as catalyst for the SMC in water.[78]

Trzeciak and co-workers reported palladium supported on triazolyl-functionalized polysiloxane **61**, **62** as a recyclable catalyst for the SMC of aryl bromides with phenylboronic acid at 60 °C in a 2-propanol-water mixture (Figure 1).[79] In recycling experiments, very good results were obtained in eight consecutive runs.

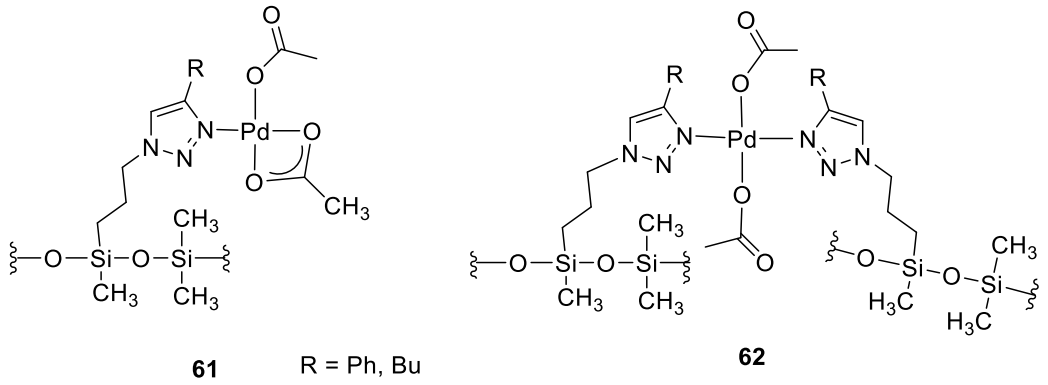
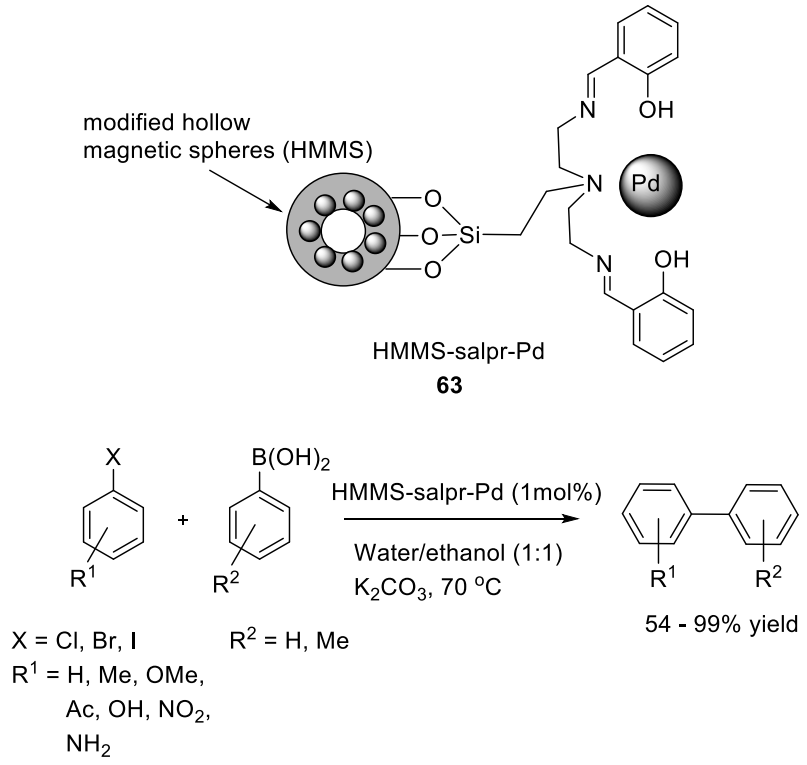


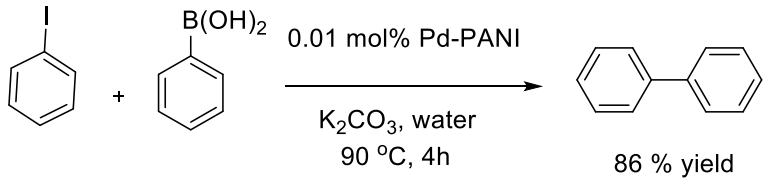
Figure 1 Triazole-functionalized siloxane co-polymers as suppors for palladium-catalyzed SMC.[79]

To overcome less accessible active sites for immobilized or supported palladium catalysts, Ma and co-workers recently developed a self-supported hollow material with tunable cavities. This material is potentially interesting thanks to its inherent features including: i) high surface area, ii) low density iii) easy recovery, iv) low cost, and v) surface permeability. Relying on tetrabutylphosphonium bromide (Bu_4PBr) as template, Ma prepared a mesoporous Pd–Fe alloy magnetic spheres catalyst with a hollow chamber.[81] This catalyst displays high activity in the SMC. In a subsequent study, Ma reported a high-performance palladium catalyst **63** resulting from the covalent anchoring of a Schiff-base ligand, *N,N'*-bis(3-salicylidenaminopropyl)amine (salpr), on the surface of hollow magnetic mesoporous spheres (HMMS) followed by immobilization of Pd(0) (Scheme 43).[80] The heterogeneous catalyst could readily be recovered from the reaction mixture and recycled six times without any loss of activity.



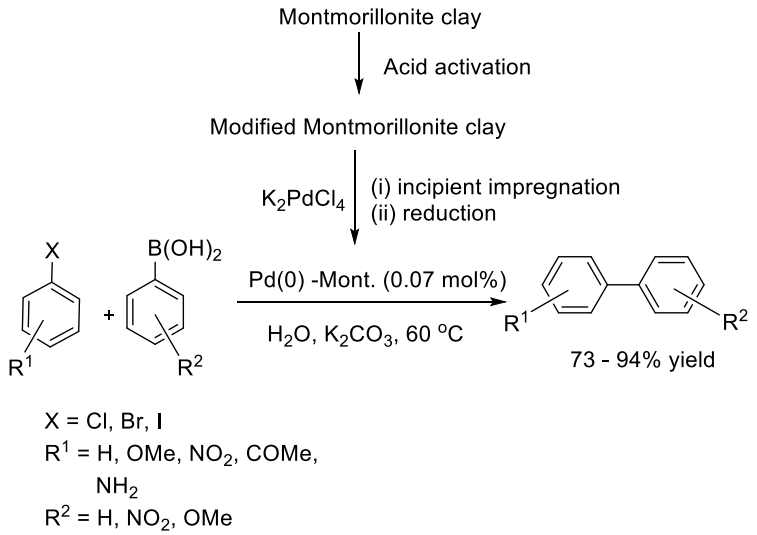
Scheme 43 Pd nanoparticles immobilized on modified hollow magnetic spheres (HMMS) for SMC in water developed by Ma.[80]

Recently, Siril and co-workers reported a palladium–polyaniline (Pd–PANI) nanocomposite for the SMC in aqueous media (Scheme 44).[82] PANI is a conducting polymer which was used as a catalyst support. With this system, they showed that the SMC proceeds much faster in water than in toluene.



Scheme 44 Palladium-polyaniline nanocomposite for SMC in water.[82]

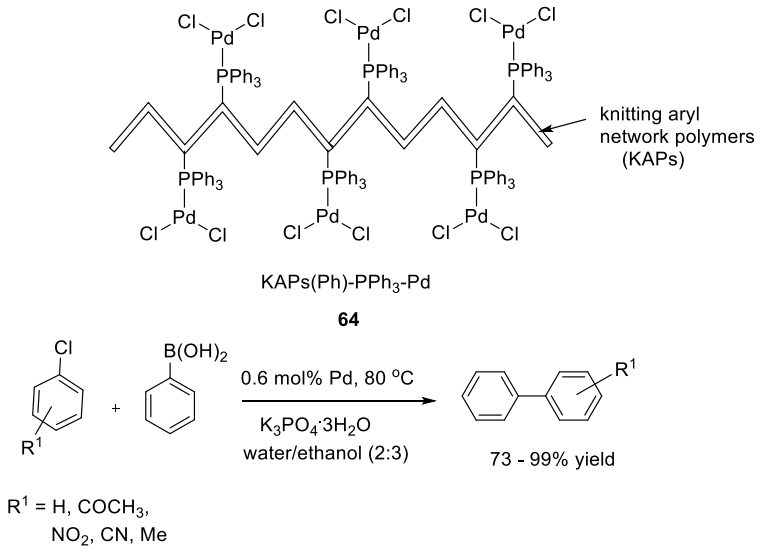
Dipak and co-workers reported on the application of the modified Montmorillonite clay supported Pd(0)-nanoparticles as an efficient catalyst for the SMC (Scheme 45).[83] This naturally occurring clay requires no surface functionalization and its pore sizes can be tuned by an acid activation. The modification of Montmorillonite clay was carried out by activating with H_2SO_4 under controlled conditions to generate nanopores on the surface, thus serving as a 'Host' for the Pd(0)-nanoparticles. The supported Pd(0)-nanoparticles were efficient catalysts for the SMC (up to 94% yield) in water under ligand free conditions. The nano-catalyst could be recycled at least three consecutive runs with a little loss of catalytic activity.



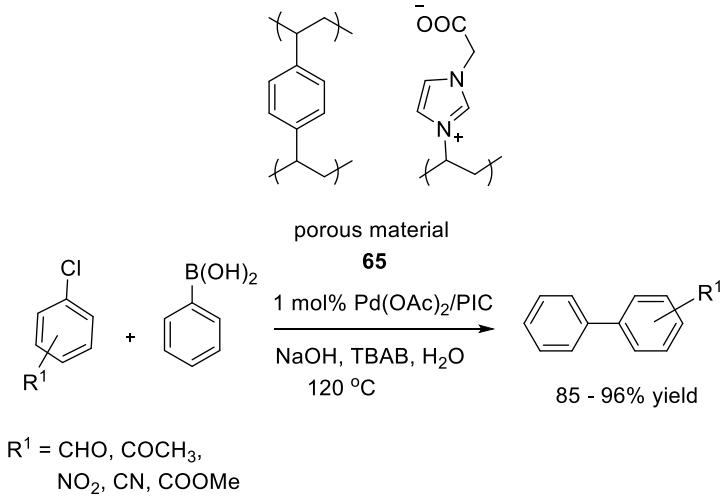
Scheme 45 Pd(0)-Montmorillonite clay composites catalyzed SMC in water.[83]

Recently, Li[84] reported on a highly dispersed palladium chloride catalyst anchored in triphenylphosphine-functionalized knitting aryl network polymers (KAPs) **64**. These exhibited excellent activity for the SMC of aryl chlorides in aqueous media (Scheme 46). A potential reason for high catalyst activity was that the microporous

polymers not only played the role of support, but also protected the Pd(0) species from aggregation and precipitation.



Scheme 46 Aqueous SMC catalyzed by KAPs(Ph-PPh_3)-Pd.[84]

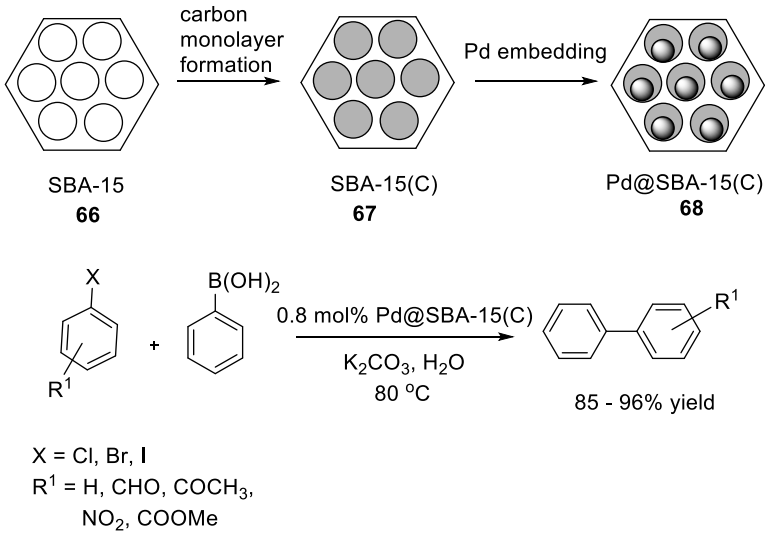


Scheme 47 A $Pd(OAc)_2$/porous ionic copolymer (PIC) catalyzes the SMC in water.[85]

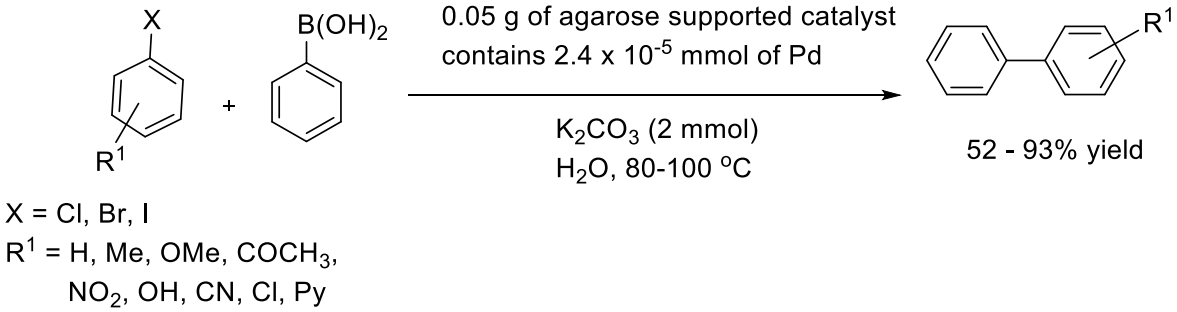
Huang and co-workers reported on the use of Pd nanoparticles on a porous ionic copolymer **65** of an ionic liquid and divinylbenzene for the coupling of aryl bromides

and chlorides under air and in water, using Pd loadings as low as 10 ppm (Scheme 47).[85]

Hu and co-workers embedded Pd nanoparticles in carbon thin film-lined nanoreactors **67**. The resulting embedded nanoparticles **68** catalyzed the SMC yielding good results, allowing the recycling of the heterogeneous catalyst (Scheme 48).[86] Thanks to their controllable size, composition and morphology, mesoporous silica (e.g. SBA-15 **66**) are highly attractive supports for immobilizing Pd nanoparticles.



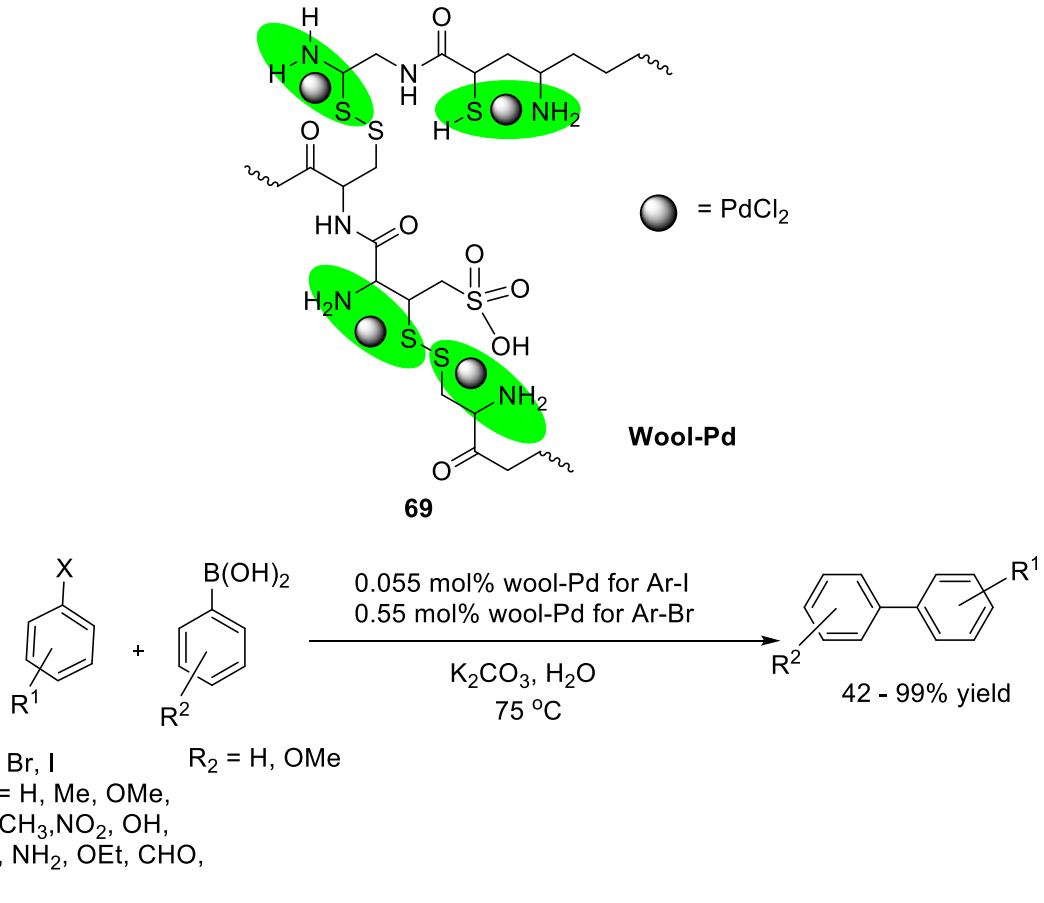
Scheme 48 Pd nanoparticles-embedded nanoreactor catalyzed SMC in water.[86]



Scheme 49 Agarose hydrogel supported Pd nano catalyst for the SMC in water.[87]

Firouzabadi and Iranpoor used an agarose hydrogel to contain the Pd for the SMC in water (Scheme 49).[87] The catalyst was efficiently recycled five times.

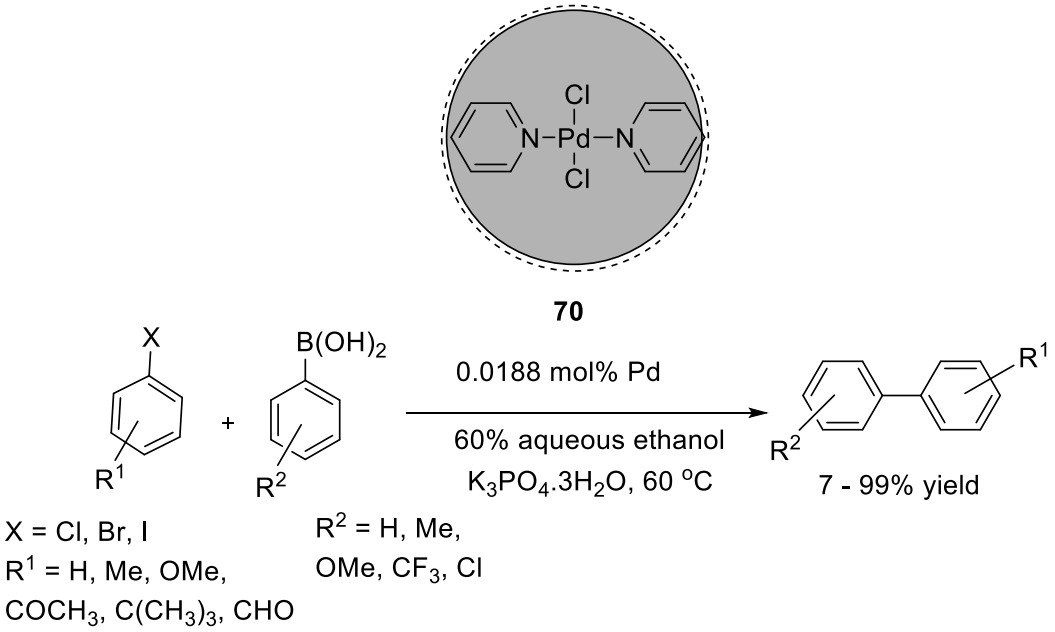
Ma and Lei prepared a heterogenous biopolymer complex consisting of wool-$PdCl_2$ **69** that performed the SMC of aryl chlorides in water (Scheme 50).



Scheme 50 A wool-Pd complex the the SMC in water.[87]

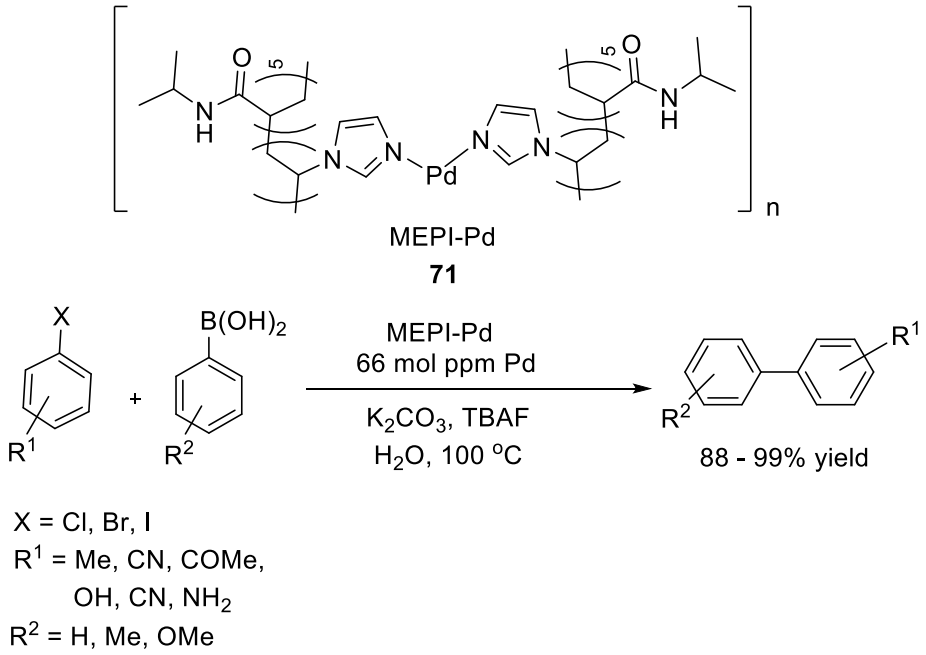
Li and co-workers used recyclable monodispersed zeolithic hollow spheres **70** containing [$PdCl_2$(pyridine)$_2$] to couple aryl bromides and iodides in a 60% aqueous ethanol solution (Scheme 51).[88] This catalyst afforded fast conversions for the SMC of various aryl halides and arylboronic acids even at Pd loadings of 0.0188 mol%.

Under mild and aerobic conditions, a TOF 63210 h^{-1} is reported. This catalyst could be recycled at least 10 times without any loss of activity.



Scheme 51 Monodisperse zeolitic hollow spheres containing $[PdCl_2(pyridine)_2]$ catalyze the SMC in water.[88]

Yamada and Uozumi[89] developed a metalloenzyme-inspired polymer catalyst **71**: a self-assembled catalyst consisting of poly(imidazole-acrylamide) and $[(NH_4)_2PdCl_4]$ that promoted the allylic arylation, alkenylation, and vinylation of allylic esters with aryl/alkenylboronic acids in water with TON varying between 20,000–1,250,000 (Scheme 52).

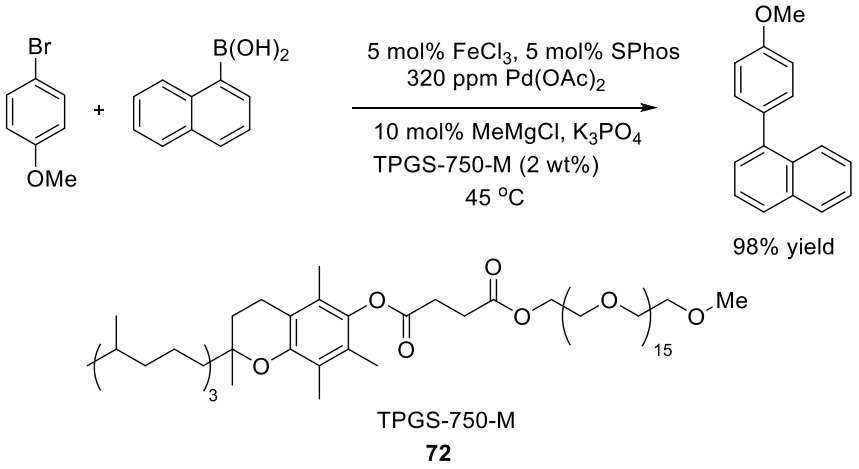


Scheme 52 A Metalloenzyme-inspired polymeric imidazole Pd catalyst (MEPI-Pd) for the SMC in water.[89]

3.2 Unsupported catalyst

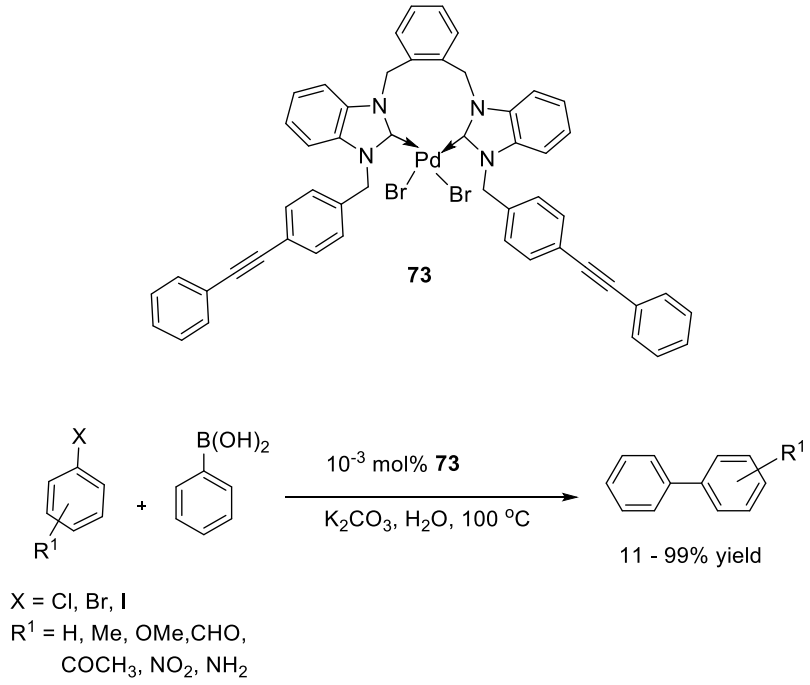
In a recent study, Lipshutz and co-workers reported that nanoparticles formed from inexpensive $FeCl_3$ that contains parts-per-million (ppm) levels of Pd catalyze the SMC in water (Scheme 53).[90] This system however requires the use of designer surfactant TPGS-750-M **72**. This surfactant is composed of a lipophilic α-tocopherol moiety and a hydrophilic PEG-750-M chain, joined by an inexpensive succinic acid linker, spontaneously forms micelles upon dissolution in water.

NHC-ligands are very common in homogeneous catalysis (*vide supra*), although they are rarely used in heterogeneous catalysis to stabilize Pd(0). Recently, Schmitzer used an unsupported Pd-NHC complex **73** for SMC (Scheme 54).[91] The catalyst is insoluble in water and the mercury drop test suggested the heterogeneity of the



Scheme 53 Fe–ppm Pd nanoparticle catalyzed SMC in water.[90]

system. This heterogeneous catalyst was used in low loadings (10^{-3} mol%) for the SMC in pure water with very good recyclability (10 times) and high yield (TON = 10^5).



Scheme 54 Support-free palladium−NHC catalyst for SMC in water.[91]

The first ligand-free SMC of aryl halides with potassium aryl-trifluoroborates in water was reported by Molander *et al*. in 2003.[92] Following this report, many groups developed ligand free strategies for SMC in water. In this context, Bora [93] and Liu [94, 95] have recently shown that the only use of $PdCl_2$ and $Pd(OAc)_2$, respectively, in the presence of an adequate base can couple a variety of aryl bromides in water. Boruah and co-workers reported $Pd(OAc)_2$-catalyzed SMC of aryl bromides with arylboronic acids in aqueous tea extract at room temperature.[96] Recently, Corma and co-workers developed palladium clusters with three- or four palladium atoms (characterized by UV–visible spectroscopy) which were found to be the catalytically active species (3-300 ppm Pd, TOF up to 10^5 h^{-1}) for the SMC.[97] These palladium cluster could be stabilized in water and stored for long periods of time for use on demand with no loss of activity. Qiu and Xu reported Pd–Pt nanodendrites for a ligand free SMC in an ethanol-aqueous solution.[98] Liu and co-workers reported an aerobic, ligand-free SMC catalyzed by Pd/C (3 mol%) in aqueous media.[99] Control experiments demonstrated that the Pd/C-catalyzed the SMC was much quicker when performed in air or oxygen (98% yield in 30 minutes) than under nitrogen (62% yield in 40 minutes). Deveau and coworkers[100] reported synthesis of Ethyl(4-phenylphenyl)acetate, a biaryl with anti-arthritic potential using $Pd(OAc)_2$ with no additional ligand in aqueous acetone (0.5 mol% catalyst loading, 90% yield). Liu and co-workers reported the SMC of potassium aryl-trifluoroborates with aryl bromides in water using $Pd(OAc)_2$ as a catalyst (1-3 mol%) with $[bmim]PF_6$ ionic liquid as an additive and Na_2CO_3 as a base under air.[101] They obtained biaryl products up to 99% yield in 2-3 hours. Sarma and Saikia reported recently a recyclable $Pd(OAc)_2$

catalyzed SMC in neat "Water Extract of Rice Straw Ash" (WERSA) at room temperature.[102] They obtained 45 – 90% yield for the synthesis of biaryl product with 1 mol% Pd loading.

Palladium nanoparticles (Pd-NPs) are nowadays widely used in catalysis and have become a strategic tool for organic transformations, thanks to their high catalytic activity. Pd-NPs are valuable alternatives to molecular catalysts as they do not require costly ligands. Astruc and co-workers showed that the SMC of aryl chloride proceeds efficiently in water (or in organic-water mixtures) at high temperatures with ppm amounts of Pd-NPs.[103]

Veisi and coworkers reported palladium nanoparticles (Pd-NPs) stabilised by *Pistacia atlantica kurdica* (*P. a. kurdica*) gum as catalyst for the SMC in water.[104] The Pd-NPs were employed as a heterogeneous catalyst in the SMC at low palladium loading (0.1 mol%) under aerobic and ligand-free conditions in water. The system was characterized by moderate TONs (up to 980). The catalyst could be recycled at least eight times without loss of activity.

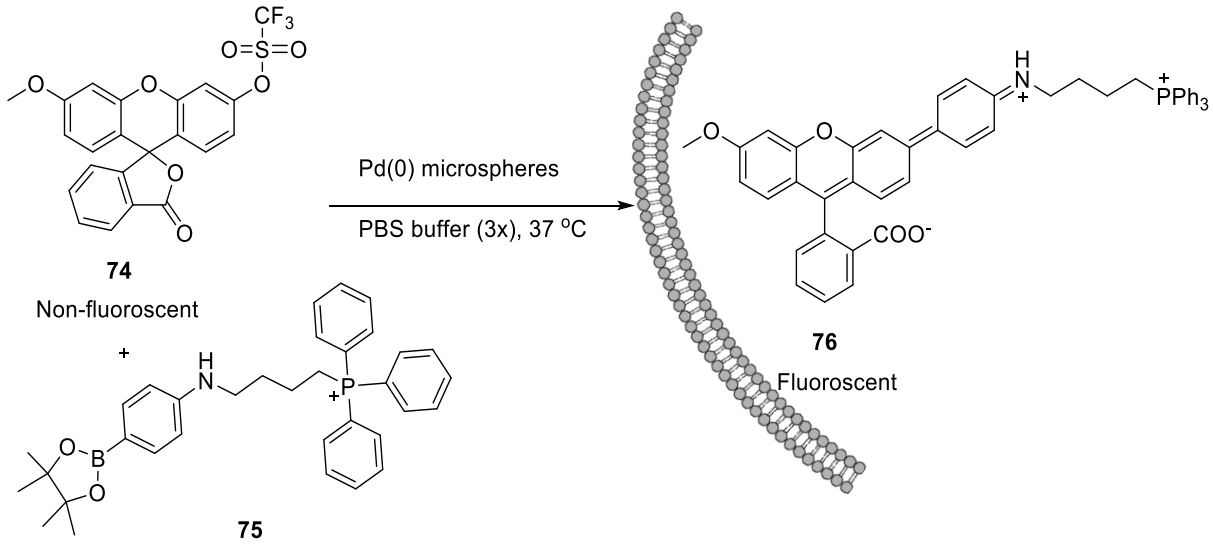
The group of Martin reported the synthesis of stable Pd-NPs generated by electrochemical methods at room temperature via the electroreduction of an aqueous solution of H_2PdCl_4 in the presence of PVP (xxx what is pvp).[105] These Pd-NPs exhibited high catalytic activity in the SMC in aqueous medium. Particularly high turnover numbers (TON 10^4 - 10^5) were achieved with aryl iodides and bromides. Recently, Pore and co-workers reported ionic liquid promoted in situ generation of palladium nanoparticles (particle size between 3-9 nm) which efficiently catalyzed

SMC in water.[106] With 2 mol% $Pd(OAc)_2$ and 20 mol% ionic liquid, they achieved upto 98% yield at 80 ^oC. The aqueous system containing ionic liquid along with Pd-NPs could be recycled seven times with any loss of activity. Maitra and co-workers reported hydrogel-stabilized palladium nanoparticles for SMC in water.[107] They obtained upto 90% yield for biaryl synthesis with 0.15 mol% Pd loading. Recently Tang and co-workers reported Pd-NPs supported and stabilized by mesoporous graphitic carbon nitride (g-C_3N_4).[108] The SMC proceeded smoothly with 97 % isolated yield (0.83 mol% Pd loading) in less than 30 minutes in water with PEG600 as the additive. Gholinejad and co-workers[109] reported a polymer containing phosphorus–nitrogen ligands for stabilization of palladium nanoparticles which was an efficient and recyclable catalyst for SMC in neat water. The biaryls products were obtained upto 99% yield with 0.08 mol% Pd loading in presence of ^{t}BuOK as a base. Liu and coworkers[110] developed a palladium-catalyzed ligand-free SMC of heteroaryl halides with *N*-methyliminodiacetic acid (MIDA) boronates in excellent yields (up to 96%) with 2 mol% Pd loading.

3.3 Heterogeneous SMC for Chemical Biology Applications

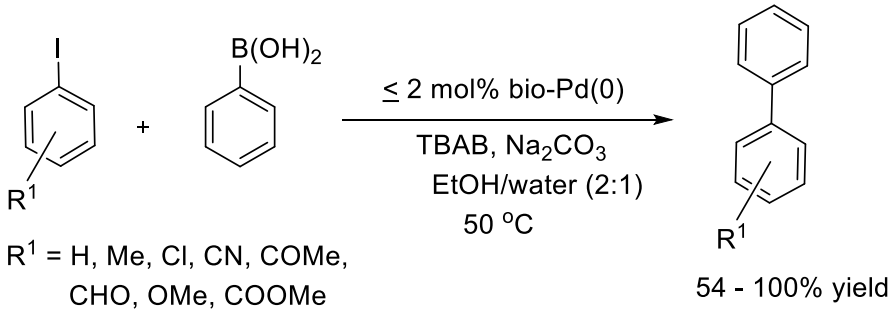
The first use of the SMC in mammalian cells was reported by Bradley and co-workers.[56] They trapped palladium nanoparticles within inert polymeric microspheres, with the catalysts derived from a recyclable, ligand-free heterogeneous palladium precursor. The resulting polystyrene microspheres were employed as 'Trojan-horses' to deliver the palladium nanoparticles into a cell, allowing to perform a SMC of **74** and **75** to afford the fluorescent product **76** *in cellulo* (Scheme 55). [64,

65] They used almost stoichiometric amount of catalyst and there is no mention of yield or TON in corresponding paper.



Scheme 55 Palladium nanoparticles encapsulated within inert polymeric microspheres as catalyst for the SMC *in cellulo*.[56]

The research group of Parker demonstrated that Pd(0)-nanoparticles produced by living plants displayed excellent catalytic activity in the SMC.[66] Certain strains of bacteria (e.g. *Desulfovibrio desulfuricans, E. coli and Shewanella oneidensis*) can reduce soluble Pd(II) from stock solutions or acid extracts of spent catalysts, forming metallic palladium nanoparticles. This protocol involves biosorption of Pd(II) cations on the surface of bacteria and a subsequent reduction to Pd(0) using an electron donor. The formed nanoparticles are supported either on the bacterial outer-membrane or in the periplasmic space and remain attached to the cells ("bio-Pd(0)"). Skrydstrup and coworkers[69] reported that the SMC can be catalysed by bio-generated palladium nanoparticles formed on the surface of Gram-negative bacteria (Scheme 56).



Scheme 56 "bio-Pd(0)" catalyzed SMC developed by Skrydstrup and coworkers.[69]

Biological macromolecules have gained significant attention as alternative template materials for the generation of well-dispersed metal nanoparticle via electroless deposition. Yi and coworkers[68] demonstrated that the tobacco mosaic virus (TMV) is a suitable support for the generation of immobilized palladium (Pd) nanocatalysts which are active for the SMC in water.

4 Outlook

In a green chemistry spirit, aqueous SMC has enjoyed an exponential growth in the past four years. In many cases however, the aqueous SMC require either high temperatures or the use of a co-solvent for chloride substrates. Future research will certainly be aimed to design more economical and high- performance catalysts.

Acknowledgements

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